INORGANIC CHEMISTRY

BY

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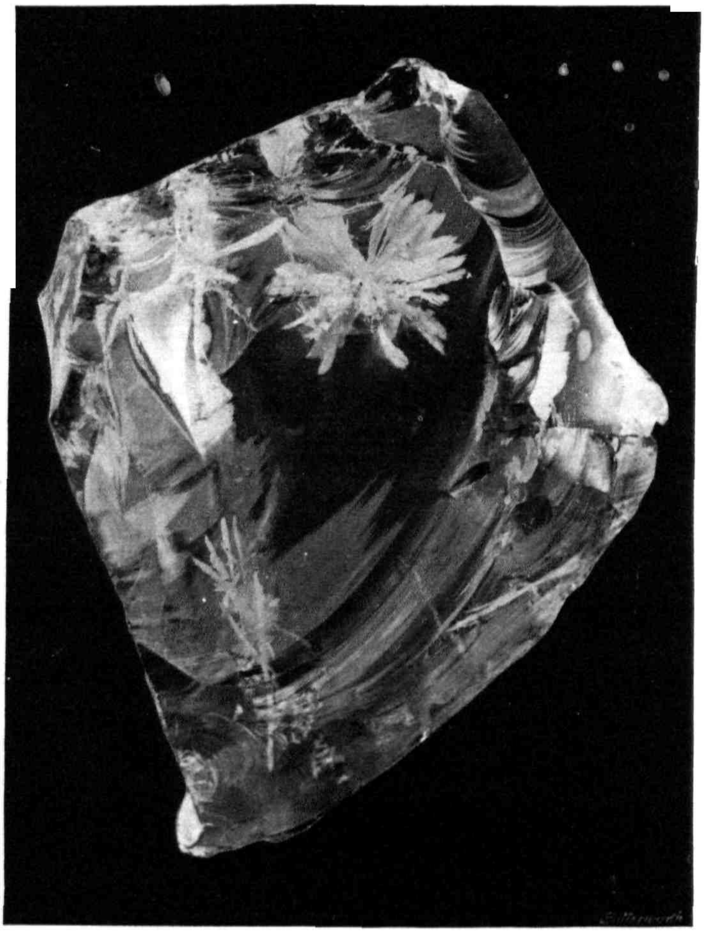

[Frontispiece

CONCHOIDAL FRACTURE AND DEVITRIFICATION OF GLASS.

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PREFACE

DURING the past fifty years the character and scope of the study of inorganic chemistry have been modified greatly by the growing influence of physical chemistry upon it. In the purely scientific aspects of the subject, the mere preparation and analysis of compounds have been expanded by the construction of equilibrium-diagrams showing the conditions of their formation, and their range of stability. In industry, the rugged methods of the Leblanc Soda Process have been abandoned on account of the greater efficiency of the Solvay Process; and synthetic ammonia, produced by methods which defy the principles that formerly guided the operations of inorganic chemistry, is already competing with that obtained by destructive distillation.

The change which has thus been wrought in the outlook of the inorganic chemist has made it possible to re-write many chapters of the science in the light of the fuller knowledge now available. To do this, without sacrificing other essential features of a text-book of inorganic chemistry, has necessitated the use of a larger volume than would otherwise have been necessary; but it is believed that this will not prove to be a disadvantage, as it may help to bridge the gap between the text-books studied in schools, and by elementary classes in the universities, and the larger treatises, which are as a rule used as works of reference only.

The earlier chapters are an adaptation of the author's "Historical Introduction to Chemistry," a book which was formed as a by-product in the preparation of the present volume. For convenience in revision, and to meet the requirements of students who have already taken a course in chemistry, formulæ and equations which would be out of place in describing the pioneer work of the early chemists have been given in a "Summary and Supplement" at the end of the introductory chapters. In the systematic part of the book, equilibrium-diagrams have been used freely, especially in the case of metallic alloys, and analytical data have been curtailed or omitted; important industrial operations have, however, been described, in several cases with the help of diagrams and figures specially drawn to represent modern

practice. An attempt has also been made to give a simple account of the mineral silicates which shall correspond with their fundamental importance in mineral chemistry. Purely as a matter of convenience, the metals have been divided into two groups, the "typical series" and "transition series" of Mendeléeff; this has the advantage of bringing together the metals of the alkalies, the alkaline earths, and the earths, and of associating copper, silver, and gold with the heavy metals of the transition series instead of with sodium and potassium.

In compiling the book, Miers's "Mineralogy," Clarke's "Data of Geochemistry," and Greenwood's "Industrial Gases" have been used freely, in addition to the usual journals, abstracts, and works of reference. I am indebted to Dr. A. S. Russell for the chapter on Radioactive Elements, to my colleague Dr. F. W. Aston for a section on Isotopes, to Prof. W. E. S. Turner of Sheffield for a section on Glass, and to Mr. F. F. Renwick of Ilford Ltd. for a section on Photography; I have also received valuable assistance from Dr. R. W. Merriman and from Mr. W. A. Davis in drafting chapters on the non-metals and metals respectively. The chapter on Crystals has been corrected by Prof. W. L. Bragg of Manchester University, and that on Silicon by Dr. L. J. Spencer, of the Natural History Museum, South Kensington. The paragraph on Cement has been corrected by Mr. S. G. Pannisett of the Portland Cement Research Association, that on Light Alloys by Dr. W. Rosenhain, and the other metallurgical sections by Prof. C. H. Desch of Sheffield. I am under particular obligation to the late Dr. J. C. Cain, Editor of the Chemical Society's Journal, for reading through the whole of the proofs; these have also been read by Prof. K. C. Browning, Dr. P. C. Austin, Mr. A. Greeves, and Mr. H. McCombie, to whom I owe the correction of a number of errors.

Nearly all the photographs are the work of Mr. W. Butterworth; but I am indebted to the Skinningrove Iron Co. for a new diagram of a blast-furnace plant and to Brand's Pure Spelter Co. for a drawing of a zinc furnace. Several equilibrium-diagrams have been drawn specially for this book; others have been adapted from Landolt-Bornstein's Tables; the crystal-drawings are after Miers and Groth.

Finally, I wish to express my appreciation of the valuable advice and assistance given by Sir Richard Gregory and by the late Mr. A. T. Simmons during all the stages of production of the volume.

T. M. Lowry.

January, 1922.

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PART I.—HISTORICAL AND INTRODUCTORY

CHAPTER I

RAW MATERIALS AND PURE SUBSTANCES

Pure Substances and Mixtures.

Chemistry is concerned largely with the study of the properties and behaviour of pure substances when examined either separately or in the form of mixtures. An important part of the work of the chemist consists therefore in separating pure substances from the raw materials provided by nature, and in testing his products in order to find out whether they have been properly purified or not.

THE STATES OF MATTER.

Raw Materials: Gaseous, Liquid, and Solid.

The raw materials with which the chemist works may occur as gases, liquids, or solids, and the processes adopted for separation and purification differ widely in these three cases. It is therefore desirable to consider the properties of matter in its different states as an introduction to the main problem of purification.

(*a*) *Gases and Vapours* were described by Robert Boyle in 1660 as "elastic fluids." Their chief characteristic is their ELASTICITY, which causes them to expand whenever the pressure upon them is diminished. A gas or vapour will therefore always fill the vessel which contains it, and will exert on the walls of the vessel a pressure, which diminishes, however, when the volume of the gas is increased. Conversely, if the volume be diminished the pressure will increase; but in the case of many gases a point is reached, sooner or later, at which any further increase of pressure causes the gas to collapse and to condense as a liquid; gases which can thus be liquefied by pressure alone are commonly distinguished as VAPOURS.

(*b*) *Liquids*, like gases, are fluids. Their FLUIDITY enables them to alter their shape to conform with the vessel in which they are contained; but, unlike gases, they have a definite volume and need

that at a particular moment the movement of the boundary indicates the conversion of a given particle of water into ice.

What, then, is the essential difference between water and ice that makes it possible to recognise so sharp a boundary in temperature, in space, and in time? It is this, that ice is "crystalline" and water is not. The main feature of a CRYSTAL (Greek κρύσταλλος, from κρύος, icy-cold) is the orderly arrangement of the component particles. In a gas, the particles move so rapidly that it is impossible for any orderly arrangement to exist; even if the position of the particles could be fixed, as in an instantaneous photograph, their arrangement could only be described as *chaotic*. In a mobile liquid, the rapid movement of the particles, which enables the liquid to flow, again favours a state of chaos. In viscous liquids and glassy solids, the

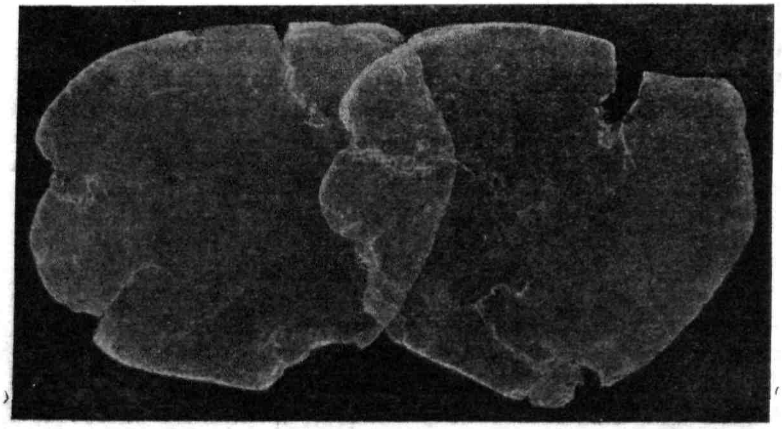


FIG. 3.—CLEAVAGE OF MICA.

particles move more slowly, but there is no directive force sufficiently strong to marshal them into regular ranks and columns. When such a force appears, and develops order out of chaos, the material is at once recognised as crystalline.

Whilst, therefore, it is not easy to draw a sharp distinction between gas, liquid, and solid, it is possible to classify substances much more rigidly into two groups, as (*a*) CRYSTALLINE and (*b*) non-crystalline or AMORPHOUS (Greek ἄμορφος, from ἀ, without, μορφή, form).

Properties of Crystals.

(*a*) *Structure*.—Amorphous substances are sometimes described as ISOTROPIC, that is, having the same properties in all directions (Greek ἴσος, equal, τροπή, a turning). Crystalline substances are then ANISOTROPIC because their properties differ in different directions. This

distinction is analogous to that which exists between a natural forest and an artificial plantation in which the trees have been set in regular rows.

(*b*) *Flat Surfaces and Cleavage are not essential.*—The flat surfaces of crystals, such as quartz (Fig. 11) and the alums (Figs. 8 and 9), and the regular cleavage of crystalline solids, such as mica (Fig. 3, compare also Figs. 196 and 197), rock salt, and Iceland spar (Fig. 4, compare also Figs. 231 and 232), are important manifestations of their regular structure, but are not essential characteristics of the crystalline state. A crystal, like a plantation, may have a very irregular boundary, in spite of the orderly arrangement that prevails within it.

(*c*) *Rigidity or Fluidity.*—Many crystals are extremely rigid and cannot be deformed to any extent without breaking; but other crystals are so soft that the mass can be made to flow under pressure, as in the

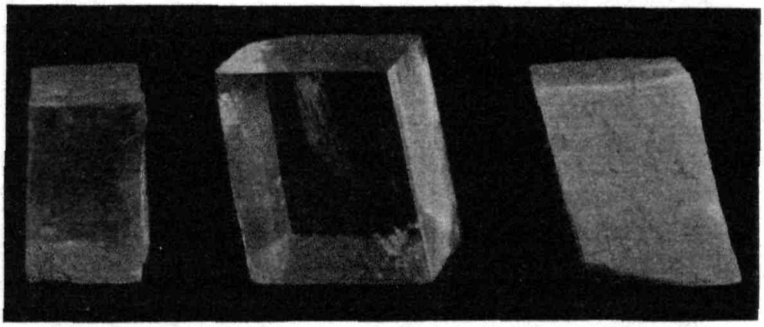


FIG. 4.—CLEAVAGE OF ROCK SALT, CALCITE, AND BARYTES.

The cleavage of rock-salt is *cubic* or *rectangular*. The cleavage of calcite or Iceland spar is *rhombohedral*, the angles over the edges of the rhombohedral fragments being 74° 55′ and 105° 5′. The cleavage of barytes is *orthorhombic*, the rhombic fragment being rectangular over some of its edges, whilst the angles of the parallelogram forming the front face of the figure are 78° 23′ and 101° 37′.

"squirting" of metallic lead through an orifice in the manufacture of lead pipes. In the limiting case of LIQUID CRYSTALS (Figs. 5 and 6) the material is so soft that it flows readily under gravity, but mere contact with two parallel surfaces, *e.g.*, a microscope slide and cover slip, causes the particles to marshal themselves in a regular manner like a regiment "falling in" on a barrack square. In general, it is found that substances are softer when crystalline than in the amorphous or glassy state, except when near the melting-point.

Equilibrium between the Different States of Matter.

The conditions of equilibrium between the different states of a pure substance are shown diagrammatically for ice, water, and steam in Fig. 7, where a normal scale of temperature is used, but the scale of

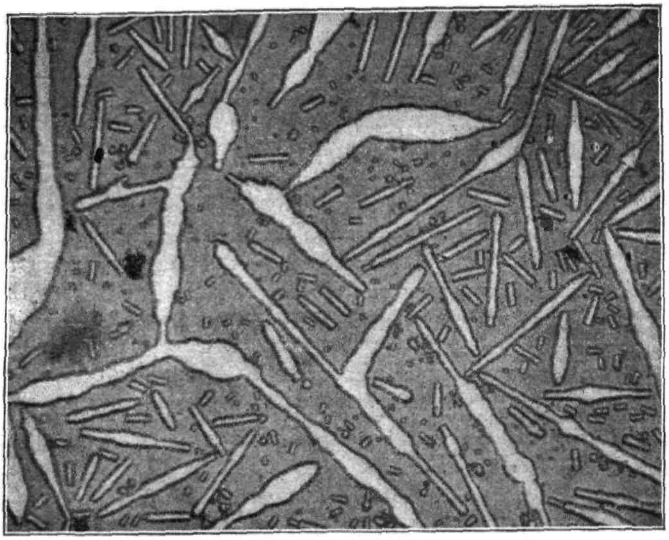


FIG. 5.—LIQUID CRYSTALS.
Notice the rectilinear form of the drops produced by suspending the liquid crystals in oil.

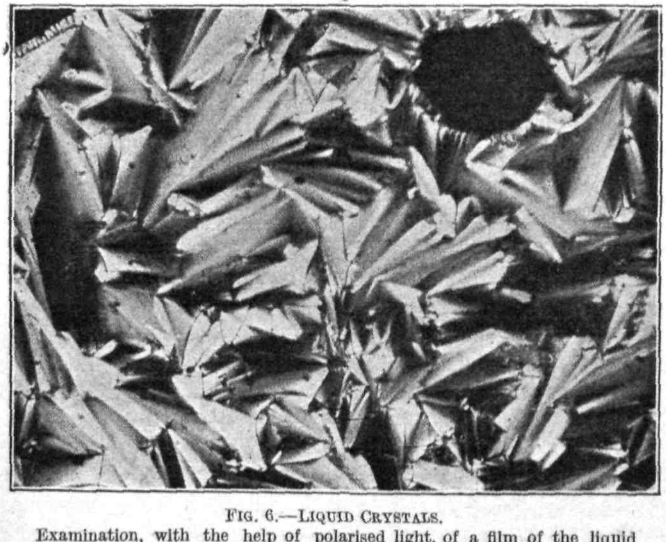


FIG. 6.—LIQUID CRYSTALS.
Examination, with the help of polarised light, of a film of the liquid pressed out between a microscope-slide and cover-glass reveals coloured patches similar to those observed in a crystalline solid.

pressures has been distorted very greatly. Four states are shown, namely:

(i) GAS, which cannot be liquefied by pressure.
(ii) VAPOUR, which differs from a true gas only in that by increasing the pressure it can be converted into
(iii) LIQUID, or (iv) SOLID.

To each state an *area* is allotted in the diagram, since it can exist over a range of temperatures and pressures. The boundaries between these areas are *lines* showing the relationship which must be maintained between temperature and pressure if two states are to co-exist. At one *point* on the diagram three areas meet, and three states of matter (namely solid, liquid, and vapour) can exist together in equilibrium.

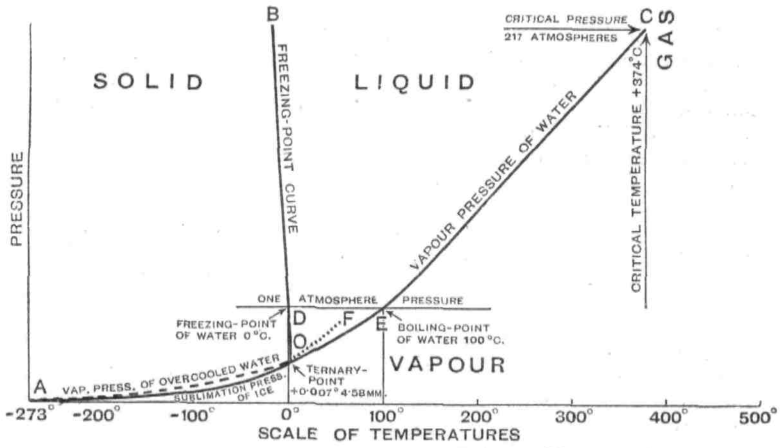


FIG. 7.—EQUILIBRIUM BETWEEN STATES OF MATTER.

(*a*) The TERNARY POINT, *O*, for ice, water, and steam is at + 0·007° and 4·58 mm. pressure; it shows the temperature and pressure which prevail when ice is melting in a vessel from which the air has been removed.

(*b*) The line *OC* (continued backwards as a broken line *OA*) shows the VAPOUR PRESSURE of water, *i.e.*, the pressure under which water boils or steam condenses at different temperatures. When the pressure is 760 mm. the boiling-point is by definition 100° C., and this point is shown at *E* in the diagram.

(*c*) At higher temperatures, the vapour pressure increases from 1 atmosphere at 100° at *E* to 217 atmospheres at 374° at *C*. Beyond this point the distinction between liquid and vapour, which becomes less and less marked as the temperature and pressure are raised, disappears completely; at this point, therefore, the vapour and liquid both pass (without any abrupt change of properties) into a gas, which will not separate into two layers unless it is cooled again below *C*. Thus, whilst solid, liquid, and vapour may form three layers or PHASES (p. 187) at the point *O*, only two

layers or phases can exist along OC, and only one beyond the abrupt termination of the line OC. The point C is called the CRITICAL POINT. It has two co-ordinates: the temperature above which liquid and vapour can no longer separate is called the CRITICAL TEMPERATURE, and the climax reached by the vapour pressure at this temperature is called the CRITICAL PRESSURE. The boundary which separates liquid and vapour from gas is not shown, since it does not represent any abrupt change of properties.

(*d*) Below E, the vapour pressure of water diminishes to 4·58 mm. at + 0·007°, when ice would normally appear. If crystallisation should not take place, the vapour-pressure curve would continue along the broken line OA, and this would finally represent the vapour-pressure of a hard, glassy solid instead of a mobile liquid, although there would be no abrupt change from one condition to the other. Usually, however, ice crystallises out from the liquid at O, and the dotted vapour-pressure curve for the "over-cooled liquid" gives place to the full curve showing the SUBLIMATION-PRESSURE of ice, *i.e.*, the pressure of the vapour given off at different temperatures by solid ice. Since ice is more stable than water at all temperatures below the normal freezing-point at O, it has a lower vapour-pressure than water, and the full curve OA lies below the broken curve OA. Conversely, the sublimation-curve intersects the vapour-pressure curve at O, as shown by the dotted line OF, in such a direction as to indicate that if ice could be heated above its normal melting-point, its sublimation-pressure would be greater than the vapour-pressure of water.

(*e*) The line OB shows the influence of pressure on the FREEZING-POINT of water or the MELTING-POINT of ice. Under atmospheric pressure, represented by a barometric column of 760 mm. of mercury, this temperature is by definition 0° C., since the temperature of ice melting under atmospheric pressure is taken as zero on the scale of the centigrade thermometer; this point is shown in the diagram at D. In a vacuum, the melting-point of ice is slightly higher at + 0·007°, but it is reduced to − 1° when the ice and water are under a pressure of 130 atmospheres. When the ice only is under pressure and the water is free to escape, the melting-point is lowered 1° by a pressure equivalent to about 11 atmospheres.

(*f*) Under atmospheric pressure, ice below 0° or water above 0° is in a condition of STABLE EQUILIBRIUM. Water, which when cooled carefully below 0° may be kept indefinitely, but tends to crystallise if stirred or in contact with a particle of ice, is then said to be METASTABLE. Ice which cannot be heated above 0° without melting is said to be UNSTABLE above 0°. As a mechanical analogy, it may be suggested that a brick resting on its base is stable, a brick standing on its end is metastable, since it requires a push to make it fall into a stable position, whilst a brick standing on an edge or on a corner would be unstable.

Miscibility of Gases, Liquids, and Solids

Miscibility of Gases.

It is a striking fact that *all gases will mix in all proportions.* No case is known in which gases after mixing tend to separate again into layers; such behaviour would indeed be incompatible with the fundamental definition of a gas, as a fluid which fills the vessel that contains

it whether other gases are present or not. Thus every gas which escapes into the atmosphere will remain there permanently, unless there are special circumstances which cause it to be destroyed or removed. It follows that when a chemist employs a gas as raw material, he must expect to find that he is dealing with a complex mixture. This mixture may include, not only gases, but also vapours derived from volatile liquids and solids. Thus, atmospheric air (p. 364) contains considerable amounts of water-vapour in addition to nitrogen, oxygen, carbon dioxide, helium, neon, argon, xenon, krypton, and hydrogen.

Miscibility of Liquids.

Unlike gases, liquids do not always mix together. Three different cases may be recognised :—

(i) Some liquids, such as oil and water, float one upon the other without mixing and if shaken up separate again completely into two layers.

(ii) Other liquids may be mixed partially. Thus at 25° water will dissolve 5·8 per cent. of ether, and ether will dissolve 1·3 per cent. of water ; but when the two liquids are mixed in any proportion between these limits (that is, water 94·2 per cent. to 1·3 per cent., ether 5·8 per cent. to 98·7 per cent.) two layers are formed, the upper layer being a saturated solution of water in ether containing 1·3 per cent. of water, and the lower layer a saturated solution of ether in water containing 5·8 per cent. of ether.

(iii) Other liquids, such as alcohol and water, may be mixed in all proportions just as in the case of gases.

Solvent Properties of Liquids.

In addition to mixing with one another, liquids are able to dissolve both gases and solids, thereby bringing them for the time into the liquid state. Broadly speaking, it might be expected that gases which are easily liquefied by cooling would be liquefied easily by dissolution, and that easily fusible solids would be readily soluble. In practice, however, dissolution is influenced much more by the chemical nature than by the physical properties of the liquid and of the gases and solids which are brought into contact with it.

This fact is expressed in the common rule that " like dissolves like " ; thus, water, which contains 8/9 of its weight of oxygen, is an excellent solvent for acids, alkalies, and salts, most of which contain either oxygen or related elements, whilst carbon-compounds are dissolved most readily by " organic solvents," that is, by liquid compounds of carbon.

Complex Character of Natural Waters and of Crude Petroleum.

On account of the solvent properties of water for gases and solids all natural waters are complex mixtures which have become

saturated with the gases of the atmosphere, and also contain mineral matter dissolved from the soil. RAIN-WATER, just condensed from the vapour of the atmosphere, contains little but gaseous impurities and may retain a high degree of purity if it should fall upon rocks which do not dissolve readily. SEA-WATER, on the other hand, must contain, not only gases, but also every kind of mineral impurity that the water has been able to wash out from the rocky surfaces of the earth during countless ages. Thus, as soon as sea-water is boiled, gases begin to escape and a cloud of CHALK is deposited; small crystals of GYPSUM are next formed; further evaporation causes the liquid to deposit COMMON SALT, EPSOM SALTS, and other salts, still leaving in solution constituents which are so soluble that they do not crystallise readily. The salt-beds of Stassfurt, which have been formed by the natural evaporation of sea-water, contain not less than thirty crystalline salts.

Crude PETROLEUM (Latin *petra*, a rock, *oleum*, oil) is an equally complex mixture, which differs from sea-water in that it contains a large number of liquid constituents in addition to dissolved gases and solids. When the pressure is released or when the liquid is heated, the gases are driven out first as NATURAL GAS. A series of liquid fractions can then be collected, which increase progressively in boiling-point as distillation proceeds; these are described successively as PETROL, PARAFFIN, CREOSOTE OIL, and LUBRICATING OIL. Towards the end, fractions are obtained which solidify partially or wholly on cooling and are sold under the names of MINERAL JELLY and PARAFFIN WAX.

Segregation of Solids.

In the case of crystalline solids, it is the exception rather than the rule for mixing to take place even under the most favourable conditions. Thus the different components of sea-water, although perfectly blended in the liquid state, separate almost perfectly when the liquid is allowed to crystallise. In metallurgy, this separation is spoken of as SEGREGATION, and this term may also be applied in the case of substances other than metals. It implies that when the solvent is removed each particle of salt seeks out other particles of salt and unites with them to form salt crystals. In the same way, particles of gypsum collect together to form crystals of gypsum, particles of Epsom salts to form crystals of Epsom salts, and so forth. When crystallisation is slow, the process of segregation leads to the formation of small numbers of large crystals; when crystallisation is rapid, many small crystals are formed; in extreme cases, the segregation may be on so minute a scale that it is difficult to recognise the separate components except by magnifying greatly. Nevertheless, crystallisation of a liquid mixture nearly always results in a sharp separation or segregation of the liquid into different solid components.

not fill more than a part of the containing vessel. When compressed, they are found to be highly elastic, *i.e.*, they offer a great resistance to forces tending to diminish their volume. When the pressure is released, they recover their original volume, but do not expand beyond it, except by passing into the state of vapour. A liquid which does not fill the containing vessel therefore exposes a "free surface" to the vapour, whereas the surface of a gas always coincides with that of the vessel in which it is confined. The forces which hold a liquid together tend to diminish its surface; the liquid therefore behaves as if it were enclosed in an elastic skin, the expansion of which is resisted (as in blowing a soap bubble) by a force which is known as SURFACE TENSION.

(*c*) *Solids* differ from liquids in that they are not fluid, and do not adapt themselves to the shape of the vessel which contains them. In virtue of their RIGIDITY they strive to preserve their shape as well as their volume and thus possess two distinct types of elasticity.

Continuity of State.

The distinction between gas, liquid, and solid is not so sharp as might appear at first sight. Thus, when the pressure is sufficiently great, there is no difference at all between gases and liquids, except that they behave differently when the pressure is released. This may be illustrated in the case of the "carbonic acid gas," which is sent out under pressure in steel cylinders for use in making aerated waters. When the temperature is below 32°C.*, liquid can usually be heard splashing about when the cylinder is shaken. But when the temperature is above 32°, the contents of the cylinder are wholly gaseous and a layer of liquid is never formed. It is therefore possible to fill the cylinder under great pressure and to prove, by releasing the pressure below 32°, that the contents are liquid; or to release the pressure above 32° and to prove that the contents are gaseous. There is, however, no abrupt change in the nature of the contents when the temperature is raised through 32° without *releasing the pressure, and it is therefore possible to pass continuously* from the liquid to the gaseous state without producing any sudden change in the nature of the material.

It is even more difficult to find any sharp distinction between liquids and non-crystalline solids such as pitch or glass. PITCH, for instance, is sufficiently brittle to be broken with a hammer (Fig. 1) and may therefore be considered as a solid; but it is always sent out, like a liquid, in barrels. When the staves are knocked off, it retains the shape of the barrel for some time, but gradually settles down and flows towards the ground (compare Fig. 2). It thus behaves as a solid towards sudden shocks, but as a liquid when sufficient time is given for it to yield to the prolonged influence of weaker forces. In the case of GLASS there is the same difficulty in

* Temperatures are given in degrees Centigrade throughout.

Miscibility of Solids. Isomorphism and Polymorphism.

In exceptional cases it is found that substances which are similar, both in chemical character and in crystalline form, will blend together even in the solid state, forming perfectly homogeneous crystalline mixtures. In these mixtures the different components are blended

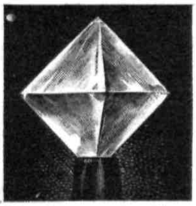


FIG. 8.—OCTAHEDRAL CRYSTAL OF ALUM.

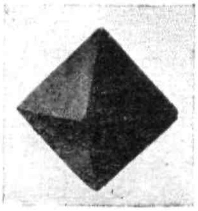


FIG. 9.—OCTAHEDRAL CRYSTAL OF CHROME ALUM.

together as perfectly as the salt and water in an aqueous solution; they have therefore been aptly described as SOLID SOLUTIONS. Substances of similar form which will blend together in this way are said to be ISOMORPHOUS (Greek ἴσος, equal, μορφή, form), and the mixed crystals are often known as ISOMORPHOUS MIXTURES. Thus, POTASH ALUM, Fig. 8, and CHROME ALUM, Fig. 9, which have the same crystalline form and are of similar chemical composition, do not separate from one another when crystallised out from water, but form perfectly homogeneous isomorphous mixtures or solid solutions, which are intermediate in properties between the two pure alums.

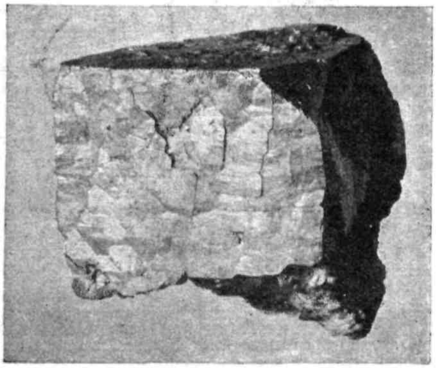


FIG. 10.—LARGE CUBE OF GALENA.
The triangular faces on the top corners are parts of an octahedron.

On account of the complex character of the magma from which they have separated, minerals are often found to be isomorphous mixtures instead of single substances; usually one main component can be recognised, but a part of its metal is replaced by other metals which form isomorphous compounds. This phenomenon is spoken of as VICARIOUS REPLACEMENT. Thus, GALENA (sulphide of lead) is isomorphous with ARGENTITE (sulphide of silver); consequently, crystals of galena (Fig. 10) that have been deposited in the presence of silver compounds may contain silver sulphide, whilst still remaining

distinguishing sharply between the liquid and solid states. When molten glass is allowed to cool, it gradually becomes more viscous

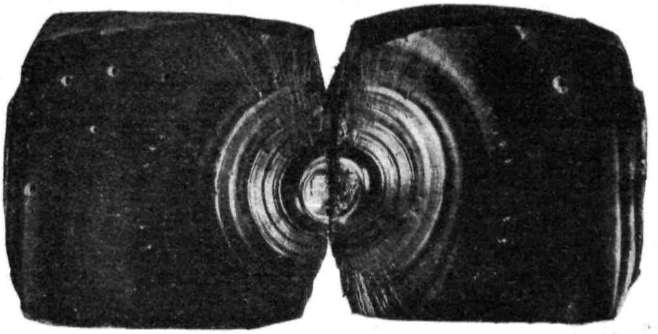


FIG. 1.—CONCHOIDAL FRACTURE OF PITCH (about $\frac{1}{3}$ full size).
The figure shows the two surfaces of a block of pitch which was split by the blow of a hammer on a chisel.

and finally brittle; but there is no sharply-defined temperature at which it can be said to pass from the liquid to the solid state. Pitch and glass may therefore be regarded as liquids which have

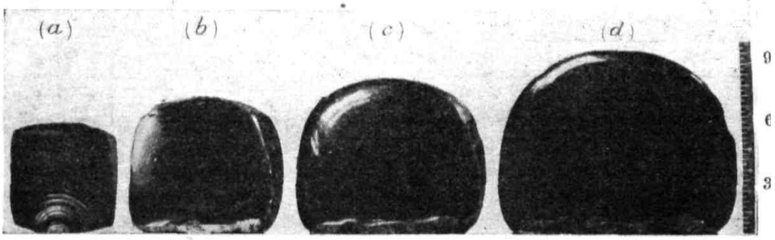


FIG. 2.—FLOW OF PITCH (about $\frac{1}{5}$ full size).
The figure shows the appearance of one half of the block of pitch (*a*) on Aug. 4, (*b*) on Aug. 10, (*c*) on Aug. 16, (*d*) on Oct. 16. No artificial heat was applied, the flow taking place spontaneously at the temperature of the atmosphere.

acquired a high degree of VISCOSITY by cooling, and have thus lost almost completely the fluidity which they possessed when hot.

The Two States of Matter: Crystalline and Amorphous.

During the CRYSTALLISATION of a liquid a change takes place which is more profound than the change from gas to liquid and much more definite than the change from liquid to glassy solid. Thus, when pure water freezes it does so at a temperature which is so sharply defined that it is used everywhere as a "fixed point" for scales of thermometers. There is an equally sharp boundary in space and in time; the water does not change all together as in the case of glass, but the ice grows at the expense of the water in such a way

perfectly homogeneous; when the ore is smelted the silver is reduced to the metallic state along with the lead, and appears as a valuable impurity in the metal.

The converse phenomenon to isomorphism, where two or more substances have the same crystalline form, is that of POLYMORPHISM, where a single substance can exist in two or more different forms, each representing a different arrangement or marshalling of the molecules in the crystal. Each type of crystal is usually stable, like water or ice, over a range of temperatures and pressures; thus, QUARTZ (Fig. 11) changes into TRIDYMITE when heated above 870°, and into CRISTOBALITE when heated above 1470°, just as ice changes into water when heated through 0°; and provided that the temperature is not too high

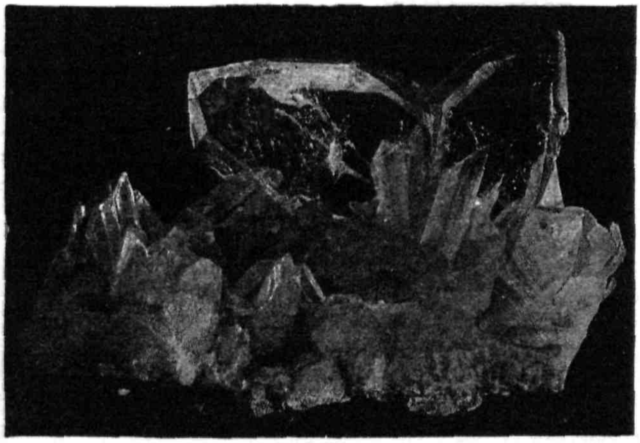


FIG. 11.—CRYSTALS OF QUARTZ.

ordinary LIGHT ICE changes abruptly, when the pressure is increased sufficiently, *e.g.*, to 2500 atmospheres at − 20°, into a DENSE ICE (p. 249) which is heavier than water.

Purity of Natural and Artificial Crystals.

On account of the great tendency for solid compounds to segregate into separate crystals, these crystals often attain a very high degree of purity. Common ROCK SALT, for instance, even when slightly coloured, is a remarkably pure material. Common LUMP SUGAR is almost equally pure, containing not more than about 0·1 per cent. of other substances. There is probably nothing in Nature that approaches more nearly to the ideal of perfect purity than a fine specimen of QUARTZ or ROCK CRYSTAL (Fig. 11); "pure as crystal" is indeed a very suitable phrase, when applied to a substance which may be almost invisible even in columns up to half a yard in

length. Even when impurities are present in a well-formed crystal, they are restricted to a small group of closely-related compounds isomorphous with the main constituent. Thus, one alum may be blended with larger or smaller quantities of another alum, from which it can only be separated with great difficulty; but the blended alum may be freed very easily from impurities of every other type. In the case of sea-water, none of the constituent salts appear to be isomorphous, and the thirty minerals of the Stassfurt salt-beds are, with perhaps one exception, all chemically homogeneous substances.

Methods of Purification.

It follows from what has been said in the preceding paragraphs that the ideal method of purifying a substance will usually be to convert it into the crystalline state, and then to free it as completely as possible from the "mother liquor" or "melt" from which it has separated, and which will contain nearly the whole of the impurities. This method may be applied, not only to solids, which can be crystallised out from a liquid "solvent," but also to liquids (such as benzene, sulphuric acid, and acetic acid), which can be made to crystallise by cooling them.

Liquids are commonly purified by distillation, that is, by converting them into vapour and collecting separately the components which boil at different temperatures. This process is now applied to gaseous mixtures, which may be purified by freezing out some of the components whilst the least condensible components remain gaseous; in other cases, the whole of the gaseous mixture is liquefied and the components are then separated by fractional distillation.

Gases can be separated partially by DIFFUSION (p. 15), that is, by taking advantage of the different rates at which gases escape through small orifices or porous partitions. They may also be purified by using chemical agents to absorb the impurities; but this method of purification has been largely abandoned in favour of physical methods of purification, depending on the unequal condensibility of the different components.

A detailed account of some of the chief methods used in purifying raw materials is contained in the next chapter.

SUMMARY AND SUPPLEMENT.

1. **Raw Materials.**—The raw materials found in nature may be either
   (*a*) CRYSTALLINE or
   (*b*) AMORPHOUS, including gases, or vapours, liquids, and glassy solids.

In the former the particles are arranged in a regular manner, whilst in the latter they are chaotic.

2. **Blending of Amorphous Materials.**—Amorphous raw materials are usually complex mixtures, since
   (*a*) all GASES mix freely with one another and do not tend to separate again;

(b) LIQUIDS dissolve not only other liquids, but also gases and solids ;
(c) GLASSY SOLIDS contain the same mixed materials before and after setting.

3. **Segregation of Crystals.**—On the other hand, CRYSTALS will not usually blend with one another, since the marshalling of different types of particles is generally incompatible. Natural crystals are therefore often very pure, even when they have crystallised from a complex solution or magma.

4. **Isomorphism.**—Substances of similar crystalline form and similar chemical composition which will form SOLID SOLUTIONS with one another are said to be ISOMORPHOUS, *e.g.*,

{ Galena or lead sulphide,	PbS
{ Argentite or silver sulphide,	Ag_2S
{ Potash alum,	$KAl(SO_4)_2,12H_2O$
{ Chrome alum,	$KCr(SO_4)_2,12H_2O$.

5. **Polymorphism.**—Substances which can crystallise in more than one form are said to be POLYMORPHOUS, *e.g.*, silica or silicon dioxide, SiO_2, can exist as

(i) **Quartz,** stable up to 870° ;
(ii) **Tridymite,** stable from 870° to 1470° ;
(iii) **Cristobalite,** stable from 1470° to its melting-point at 1710°.

6. **Equilibrium between States of Matter.**—(a) In the case of a pure substance, *three phases* or layers can exist together only at one temperature and one pressure represented by a point on the p-T diagram ; thus ice, water, and steam are in equilibrium only at + 0·007° and 4·58 mm. pressure when no other substance is present in the containing vessel (compare p. 187).

(b) *Two phases* can exist together only under a definite pressure at each temperature, *e.g.*, the VAPOUR PRESSURE of water, or the SUBLIMATION PRESSURE of ice, as represented by a line in the p-T diagram. Beyond the CRITICAL POINT the two phases of LIQUID and VAPOUR become identical and are described as a true GAS.

(c) *One phase* can exist alone over a range of temperatures and pressures, as represented by an area in the p-T diagram.

CHAPTER II

METHODS OF PURIFICATION

A.—PURIFICATION OF GASES.

Diffusion.

Gases can be separated from one another partially by DIFFUSION, that is by allowing them to diffuse or escape through a porous diaphragm and collecting separately the portions which escape and are retained at the end of a given time. GRAHAM'S LAW OF DIFFUSION states that

"*The velocity of diffusion is inversely proportional to the square-root of the density.*"

Oxygen, which is sixteen times as dense as hydrogen, therefore diffuses at only one-quarter of the rate of the latter. This method was used by Lord Rayleigh for the preliminary separation of argon (density 20 when hydrogen is 1) from nitrogen (density 14); it is also used to separate the mixture of ammonia (density $8\frac{1}{2}$) and hydrogen chloride (density 18) which is produced by vaporising sal-ammoniac (p. 600).

The phenomena of diffusion can be illustrated by means of the apparatus shown in Fig. 12. Hydrogen is passed rapidly upwards into a beaker inverted over a porous pot. On account of its lightness it enters the pot much more rapidly than air can escape through the pores. Air is therefore driven out through the vertical glass tube leading down from the pot. When the pot has been filled completely with hydrogen by diffusion from the beaker, and all the air has escaped from it, the beaker is removed. The hydrogen now escapes much more rapidly than air can enter through the pores, and water is drawn up in the vertical tube, usually to a height of about 3 feet, but falls again gradually as air flows into the pot to replace the hydrogen that has escaped. A similar, but less striking experiment, can be arranged by surrounding the porous pot with a heavy gas, *e.g.*, carbonic anhydride, poured downwards into a cup or bell-jar surrounding the pot, when the more rapid escape of the air again causes the water to rise in the vertical tube.

Graham's Law of Diffusion was established by accurate experiments on the rate of escape of gases through a porous plug of plaster of Paris, or through a disc of artificial graphite 0·5 mm. in thickness, either into a vacuum or into air under reduced pressure. The same law applies to the EFFUSION OF GASES, *i.e.*, to their rate of flow through a tiny hole (*e.g.*, 0·1 mm. in diameter)

in a thin metal plate. The TRANSPIRATION OF GASES, *e.g.*, their rate of flow through long capillary tubes, is, however, influenced greatly by their viscosity, the rate of transpiration of hydrogen being only 44 per cent. of that of oxygen instead of four times as great.

Condensation.

Since separation by diffusion is very imperfect, gases are usually separated and purified by condensation to the liquid or solid state. Thus air may be freed from water-vapour by cooling it strongly; and the gases which it contains are now separated on a large commercial scale by condensing it to a liquid and submitting the liquid air to "fractional distillation" (p. 373). Methods such as these have supplanted almost entirely the chemical methods of purification which were formerly used for the preparation of pure gases.

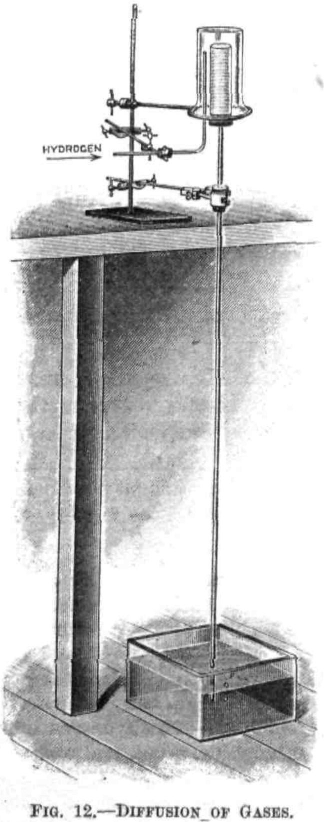


FIG. 12.—DIFFUSION OF GASES.

B.—PURIFICATION OF LIQUIDS BY FILTRATION.

General Methods.

The simplest of all methods of purifying a liquid consists in straining off the solid impurities, *e.g.*, by means of a strainer or cloth. In some cases, as in the "rendering" of fats, the crude material must first be liquefied by gently heating it. Again, it is frequently possible to do without the strainer, and merely to pour off the clear liquid from the solid that has been deposited from it; this process is known as DECANTATION.

In the laboratory, filtration is effected with the help of porous paper, the solid being drained off from the liquid by pouring the mixture on to a plain or fluted filter-paper, supported in a funnel. Filtration may be hastened by sucking away the air from beneath the filter, when the liquid is driven through it by the pressure of the atmosphere; in this case, the filter-paper is supported by a small perforated cone, *e.g.*, of platinum foil (Fig. 13), in order to prevent the point of the filter from bursting under the pressure applied to it.

Filtration with the Help of a Pump.

A more effective arrangement is that shown in Fig. 14. A perforated porcelain disc about 1½ inches in diameter is placed horizontally in the funnel and covered with two layers of filter-paper, the upper being slightly larger than the disc, so that its edges spread a little up the side of the funnel. The funnel is inserted into the neck of a strong conical flask, a rubber stopper being used to make a tight joint. Air is drawn from the flask by means of the side tube, and the solid is pressed down tightly upon the filter, so that the pressure of the atmosphere drives the liquid through the porous mass into the flask.

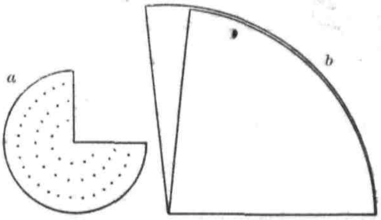


FIG. 13.—(*a*) FILTER-CONE to be fitted to funnel, (*b*) FILTER-PAPER folded so that the larger sector will fit the funnel.

The suction is produced most conveniently by means of a WATER-JET PUMP, as shown in the figure. In this pump a strong jet of water is squirted through a tiny funnel in such a way that the air in the

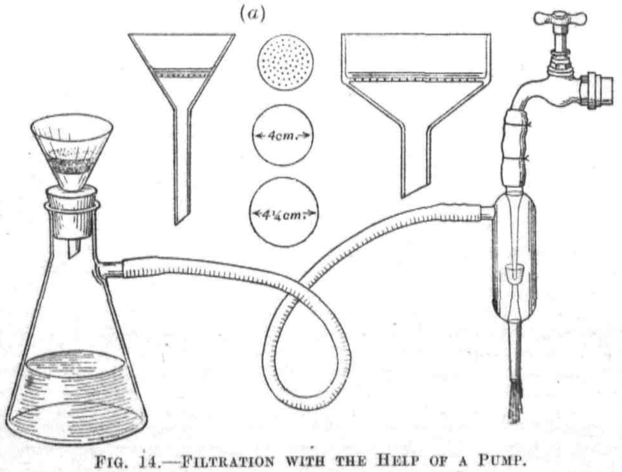


FIG. 14.—FILTRATION WITH THE HELP OF A PUMP.
The auxiliary apparatus shown in the figure includes (*a*) a porcelain filter-plate with circular filter-papers, (*b*) a Buchner funnel of porcelain with a perforated diaphragm.

funnel is carried down with the stream of water. The jet and funnel are enclosed in a glass chamber, provided with a lateral aperture which can be connected with the FILTER-FLASK by means of a thick-walled rubber tube. In this way the air carried down by the force of the jet is drawn from the flask and a remarkably good vacuum may

be produced. The use of a filter-pump is particularly advantageous when it is desired not so much to clear a liquid from its solid impurities as to collect the solid and to drain this as completely as possible free from the liquid.

Commercial Methods of Filtration.

On a large scale, the draining of a solid is effected :—

(i) By running off the liquid and allowing the solid to drain on a platform of planks or tiles ;

(ii) By sucking the liquid through layers of calico or filter-cloth in a VACUUM FILTER, or by pumping it through layers of cloth in a FILTER-PRESS under pressures much greater than those which can be produced by mere suction ; or

(iii) By putting the solid into the cage of a CENTRIFUGAL MACHINE and rotating this at a very high speed so that the liquid is spun out by centrifugal force.

C.—Purification of Liquids by Distillation.

General Methods.

The property which water and many other liquids possess of passing readily into vapour when heated is often used in order to separate them from liquids and solids which cannot be vaporised. The vapour

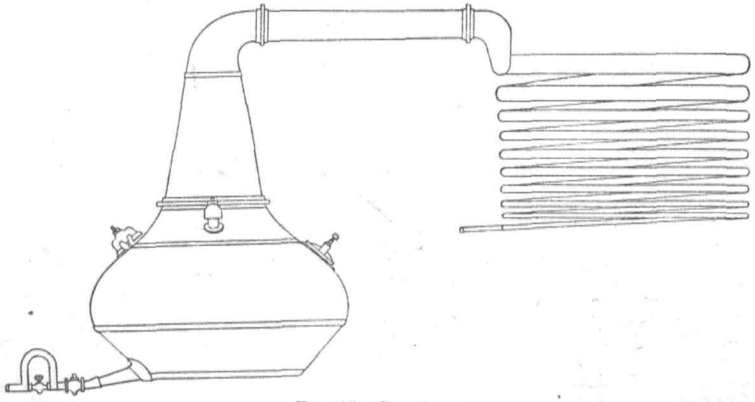


FIG. 15.—POT-STILL.

This is a large still about 12 feet in diameter. The still is provided with a revolving chain scraper to keep the bottom free from sediment. The condenser, which is immersed in water, is tapered to correspond with the condensation of the vapour.

is passed into a CONDENSER (usually a metal or glass tube cooled with water) and is there reconverted into liquid. The efficiency of the process depends (i) on holding back solid impurities which might be carried forward in the form of spray from the boiler ; and (ii) on the absence of volatile impurities in the liquid.

The commonest example of distillation is to be found in the case of water. Thus, sea-water can be rendered "fresh" (although somewhat insipid) by distilling it; distillation is also used on ships in order to provide feed-water for the boilers, which would be corroded very quickly if they were fed with sea-water. Fresh water may also be distilled to free it from chalk and other dissolved solids; DISTILLED WATER is used largely in chemical processes for which the ordinary water supply would not be sufficiently pure. Fig 15 shows the common POT-STILL as used for the distillation of whiskey, whilst Fig. 16 shows the INLAND REVENUE STILL used for distilling alcohol from beer, wine, etc., in order to determine their strength.

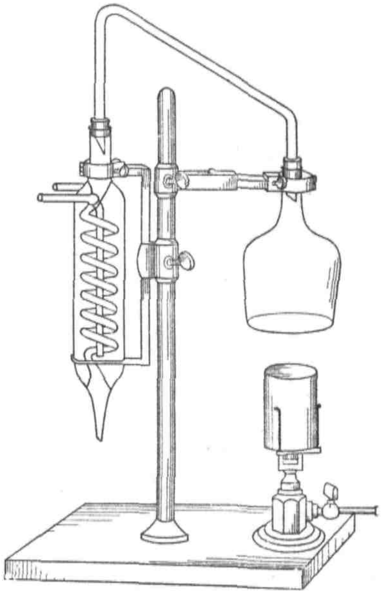


FIG. 16.—INLAND REVENUE STILL.
The tube sloping *upwards* from the flask to the condenser serves as a spray-trap to return the spray and some condensed water to the flask.

Vacuum Distillation.

The boiling of a liquid is greatly facilitated by diminishing the pressure, and thus reducing the temperature at which it boils. VACUUM DISTILLATION is particularly useful in cases in which the liquid would char or decompose if heated to the temperature necessary for distillation under atmospheric pressure; it is also resorted to when the dissolved solid is liable to char, as, for instance, in concentrating sugar syrups. An efficient apparatus for vacuum distillation on a small scale can be constructed by combining two DISTILLING FLASKS, as shown in Fig. 17, and exhausting the air by means of a water-jet pump. A few pieces of porous earthenware are placed in the liquid, and a slow stream of air is led through it by means of a capillary tube, in order to provide a constant supply of bubbles and thus to facilitate smooth boiling.

On a large scale, steam-heated VACUUM-PANS constructed of copper, or some other suitable material, are widely used. In the sugar industry, a MULTIPLE EFFECT apparatus is used (Fig. 18), in which one supply of steam is used to evaporate three or more quantities of syrup boiling under different pressures. A pan of syrup boiling under atmospheric pressure is evaporated by jacketing the outside of the pan with steam under a pressure of about 5 lb. per square inch; the steam from the first

pan is hot enough to boil the syrup in a second pan, where the pressure has been reduced by means of a vacuum pump; the steam from the second pan evaporates syrup in a third pan boiling under still lower pressure. In the case of caustic soda, four quantities of liquor may be

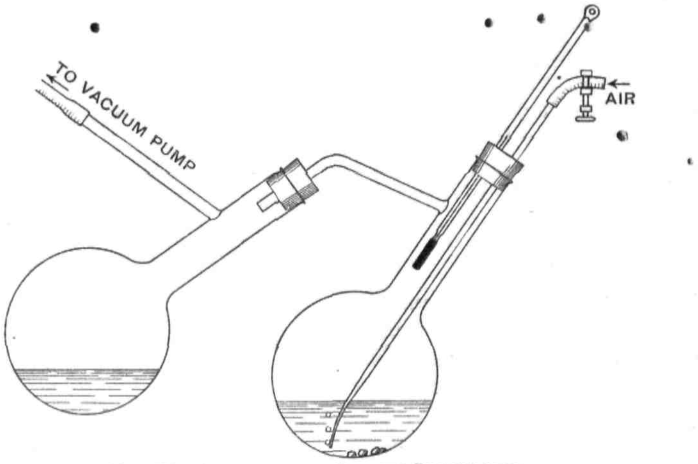


FIG. 17.—APPARATUS FOR VACUUM DISTILLATION.

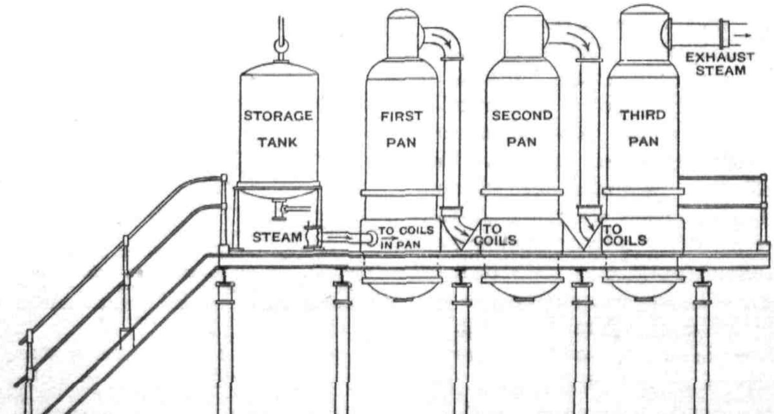


FIG. 18.—PLANT FOR TRIPLE-EFFECT DISTILLATION.
(Blair, Campbell and McLean.)

evaporated by a single supply of steam; and a similar method has recently been introduced for the evaporation of brine. In purifying water on a large scale, as many as ten stages have been used, with a corresponding economy in fuel.

Fractional Distillation.

Under some conditions it is possible, by FRACTIONAL DISTILLATION, to effect a separation of two liquids, both of which are volatile. When the two liquids differ very widely from one another in boiling-point the separation presents no special difficulties, since the whole of the more volatile constituent can be distilled and collected before the less volatile constituent begins to vaporise. When the two liquids do not differ greatly in boiling-point, both constituents are found in the vapour and only a slight separation can be effected by ordinary methods of distillation. If, for instance, the two volatile constituents of coal tar, BENZENE (boiling-point 80°) and TOLUENE (boiling-point 110°), are distilled together, the first fraction which is collected will contain a larger proportion of benzene than the original mixture, and the last fraction a larger proportion of toluene; but all the fractions will contain more or less of both constituents. A further separation can be effected by redistilling the different fractions; but as this becomes very tedious, an arrangement is adopted which effects the redistillation automatically. For this purpose, the vapour from the still is passed into the condenser through a STILL-HEAD, arranged so that any liquid condensed in it flows back again into the boiler instead of passing into the receiver. The still-head is usually cooled by exposure to the air; but sometimes it is maintained at a constant temperature intermediate between the boiling-points of the two liquids. By using an efficient still-head it is possible to separate in a single operation liquids that could scarcely be resolved at all by ordinary fractional distillation.

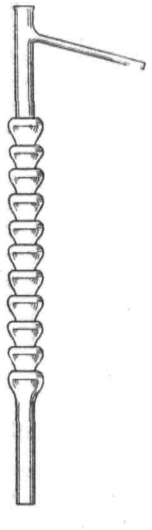


FIG. 19.

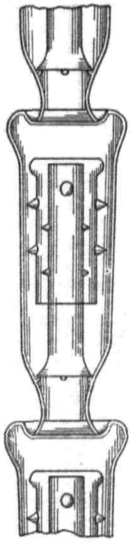


FIG. 20.

FIG. 19.—YOUNG'S PEAR STILL-HEAD. The vertical column is expanded into a series of pear-shaped chambers, in which condensed liquid drips through the ascending vapour.

FIG. 20.—YOUNG'S EVAPORATOR STILL-HEAD (about half-size). The vapour is carried by an inverted funnel to the top of a glass cover, and is compelled to pass down this before it escapes upwards into the next section. The liquid from the next section drips on to the top of the cover, and then flows down its sides in intimate contact with the ascending vapour. Evaporation of the liquid and condensation of the vapour also take place by thermal conduction through the thin glass of the cover.

Two typical still-heads (designed by Professor Sydney Young) are shown in Figs. 19 and 20. A very efficient still-head is obtained by winding a spiral of wire round a closed tube and inserting it inside a slightly wider tube (Fig. 21); the liquid and vapour then encounter each other in a long spiral path. Another simple and effective device consists in passing the vapour up a tube

or tower packed with cylindrical rings of equal diameter and height (Raschig), *e.g.*, cut from aluminium tube, or rolled from aluminium ribbon (Lessing).

The method of action of these still-heads is as follows :—A large quantity of the mixed vapour enters the lowest part of the still-head ; a small amount is condensed and returns to the still. This portion contains, in the case of a mixture of benzene and toluene, more toluene and less benzene than the vapour which passes forward, and this separation is continued in each subsequent part of the still-head. On the other hand, the descending liquid encounters the hot vapour and gives up to it some of the more volatile benzene which it contains. The efficiency of the still-head depends upon bringing the ascending vapour and the descending liquid into intimate contact, so that every opportunity is afforded for the hot vapour to drive benzene out from the liquid and for the colder liquid to condense toluene from the vapour.

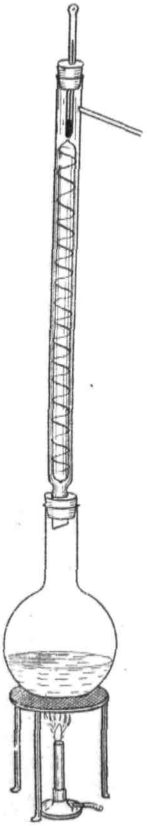


FIG. 21. DUFTON'S SPIRAL-WIRE STILL-HEAD.

The efficiency of a still-head can be shown by plotting, as in Fig. 22, the temperature of the distillate against the proportion of liquid distilled. When the fractionation is poor the curve rises continuously, and at no stage is a pure product obtained. When the fractionation is good, two large fractions are obtained, which boil constantly at the normal boiling-points of the two constituents, and the rise of temperature is confined to a small middle fraction which can either be refractionated or rejected.

Steam Distillation.

The fact that a volatile impurity may be carried over with the vapour in the process of distillation is not always a disadvantage. In STEAM DISTILLATION, this property is used in order to distil in a current of steam solids and liquids which vaporise slowly at the temperature of boiling water, but would be liable to char if distilled in the ordinary way. Water is particularly suitable for this process, since it gives an exceptionally large volume of vapour (1700 c.c. per gram) and carries over a correspondingly large proportion of the substance to be distilled. Turpentine, for instance, which boils at about 160°, may be separated from resin by a current of steam: the vapour of the turpentine passes over with the steam into a condenser, where both are condensed, whilst the resin remains behind. If the turpentine were soluble in water, the subsequent separation of the turpentine and water might be difficult; but as the two liquids do not mix, they can be separated easily by drawing off the water from beneath the turpentine. A similar process is used in separating camphor from the chopped-up twigs, wood, and leaves of the camphor tree; and also in the separation of "essential oils" from peppermint, roses, and other plants and flowers.

D.—PURIFICATION OF SOLIDS BY SUBLIMATION.

Solids Purified by Sublimation.

The property of passing into vapour is possessed not only by liquids, but also by many solids, as is shown by the fact that snow may disappear during a hard frost, although the temperature never rises sufficiently for it to melt. The direct conversion of a solid into vapour is known as SUBLIMATION. This process, as well as the distil-

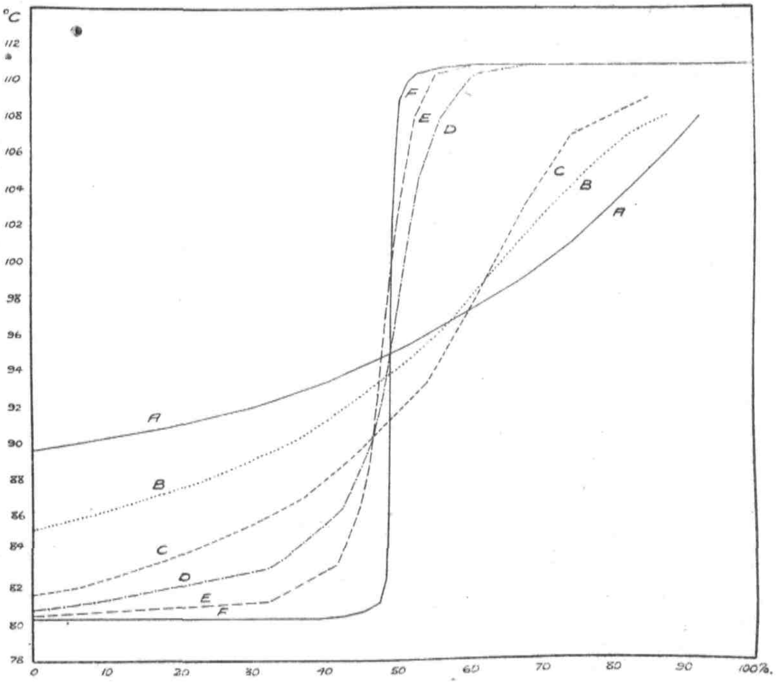


FIG. 22.—FRACTIONAL DISTILLATION (after Lessing).

A mixture of equal parts of benzene (b.-p. 80°) and toluene (b.-p. 110°) was distilled. *A*, from a distilling flask with side-tube, no still-head. *B*, through 3 bulbs 3 cm. diameter. *C*, through a column of glass beads 4 cm. diameter, 22 cm. high. *D*, through Young's evaporator still-head, 5 sections, 75 cm. high. *E*, through Young and Thomas's dephlegmator still-head, 18 sections, 130 cm. high. *F*, through aluminium rings, in tube 4 cm. diameter and 140 cm. high. In the last case, the fractionation was almost complete in one operation.

lation of easily-melted solids, is frequently used in the purification of solids. The vapour is usually cooled by passing it into a large chamber, as a condenser designed for use with liquids would speedily be blocked up if the vapour condensed to a solid when passed into it. Two examples of sublimation may be quoted: SAL-AMMONIAC, a salt-like solid, first prepared as a product of distillation of camels' dung, passes

directly from solid to vapour when heated, and may thus be separated from practically all the impurities which it contains; IODINE, which melts at 113° and boils at 184°, may also be vaporised by sublimation without previous melting. SULPHUR, which melts at 114·5° and boils at 444·5°, is purified by distilling the liquid into a large chamber in which the solid condenses as "flowers of sulphur."

E.—PURIFICATION OF SOLIDS BY CRYSTALLISATION.

Extraction with Water or with a Solvent.

A mixture of two solids, one of which can be dissolved in water whilst the other is insoluble, may be separated easily by washing the mixture with water and recovering the dissolved substances by evaporating the water. In this way, salt may be separated from sand, nitre, or saltpetre from soil, green vitriol from weathered iron pyrites, and alum from burnt alum-shale. The same process may also be employed in the case of two substances, such as salt and gypsum, which dissolve in water to widely different extents. Other solvents may also be used instead of water, as, for instance, carbon disulphide in extracting grease from wool, or ether in extracting fats from animal and vegetable products.

Fractional Crystallisation.

In the case of salts which do not differ so widely in solubility, the separation presents greater difficulties; but it is often possible by evaporating a solution containing two salts to separate and drain off a considerable quantity of the less soluble salt, whilst the whole of the more soluble salt remains behind in the MOTHER-LIQUOR. The separation of the more soluble salt presents greater difficulties; but even here it is often possible to obtain it in a fairly pure condition by judicious recrystallisation; thus when the greater part of the less soluble salt has been crystallised out, the more soluble salt may appear in a fairly pure condition in the later crops of crystals.

Other Solvents.

The purification of solids by crystallisation is not restricted to those that are soluble in water. Organic compounds which are insoluble in water are crystallised from organic solvents, such as alcohol, ether, or benzene. In exceptional cases liquids such as concentrated sulphuric acid, molten phosphorus, or a molten metal have been used as solvents for crystallisation. In some cases, no solvent at all is used. Thus, lead is purified by melting the metal and scooping out the crystals of pure lead as they separate from the melt; tin and copper are purified by LIQUATION, *i.e.*, by allowing them to crystallise and then melting away the less pure portions from the purer crystals. Sulphuric acid may be purified by freezing the crystalline acid and

draining it in a centrifugal machine. Similar methods are applied in purifying "glacial" acetic acid and "crystal" benzene; even a syrupy liquid like glycerine has been purified by crystallisation, and it is doubtful if any other method is equally efficient for the final stage in the purification of liquids.

F.—Purification of Typical Substances.

Three typical examples may be given of the methods used in separating pure substances from the crude materials from which they are derived.

(*a*) *Water*.—Water which has been distilled carefully, so that no spray is carried with the steam into the condenser, approaches very nearly to the unattainable ideal of a pure material. Distilled water should be free from solid impurities such as salt, chalk, or gypsum, but may be contaminated with traces of volatile matter, with alkali dissolved out from the glass of the distilling apparatus, and with gases derived from the atmosphere.

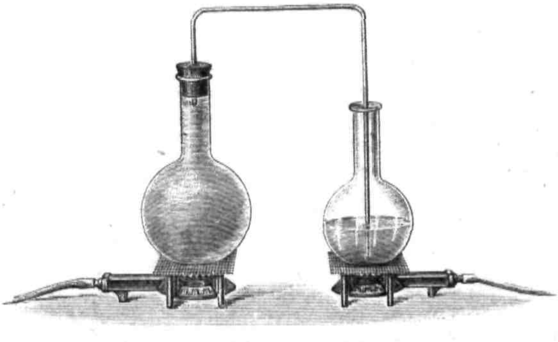


Fig. 23.—Apparatus for Preparing Water Free from Air.

Further purification can be effected by fractional distillation, the first and the last thirds of the water being rejected, and only the middle third retained. The steam should then be condensed in a vessel lined with pure tin or made of hard glass: the use of platinum or silver is not necessary. The redistilled water is stored in large bottles of hard glass. The purest water that has yet been obtained was distilled repeatedly in a vacuum, the distillate being poured back again and again, without opening the apparatus, in order to cleanse the receiver thoroughly.

Water may be freed from air by boiling it. The apparatus shown in Fig. 23 is well adapted for the purpose, since when the boiling is stopped

the water in the small flask rushes back and fills the larger flask, thus preventing the water in it from absorbing air as it cools down.

(*b*) *Alcohol*.—Alcohol, which is produced by the fermentation of organic materials containing starch and sugar, is a characteristic constituent of nearly all FERMENTED LIQUORS such as beer or wine. When these are distilled, a SPIRIT is produced which contains a large proportion of alcohol mixed with water and with small amounts of volatile oils, which impart characteristic flavours to brandy, whisky, rum, etc. By fractionally distilling these different forms of spirit, a "silent spirit" may be obtained which is practically free from all impurities except a small proportion of water. This cannot be separated by distillation, since a mixture of *alcohol* 95·59 per cent. with *water* 4·41 per cent. is more volatile than alcohol or any other mixture of alcohol and water; it can, however, be removed by boiling the alcohol with quicklime and redistilling it. The product, known as ABSOLUTE ALCOHOL, is substantially pure.

(*c*) *Salt*.—Crude salt is still prepared in some localities by evaporating sea-water either by the heat of the sun in shallow pools, or by means of artificial heat. The crude SEA SALT is obtained in coarse crystals, which may be brilliantly white, but more frequently have a grey or brown tint. It possesses the property of absorbing moisture from the air, and is therefore said to be DELIQUESCENT. It may be purified by dissolving in water, filtering from gypsum and from insoluble impurities, evaporating down until most of the salt has separated, and then draining off the liquid. The crystals of salt thus obtained should be colourless, not deliquescent, and practically pure. From the MOTHER-LIQUOR, or BITTERN, remaining after the salt has crystallised it is possible to separate several other salts, of which the most important is known as EPSOM SALTS; since common salt is not specially soluble in hot water, this separation can be carried out most conveniently by filtering off the salt from a hot concentrated solution, diluting the filtrate with a little water to prevent any further separation of salt, and setting the solution aside to crystallise. Common salt is also found in various localities in massive deposits known as ROCK SALT. Rock salt does not, as a rule, contain much gypsum, since this is found in bands which alternate with thicker layers of rock salt in the natural deposits; it is, however, purified by similar methods, and the bars of TABLE SALT prepared from it are substantially pure.

SUMMARY AND SUPPLEMENT.

1. **Gases** can be separated from one another by diffusion, the rate of which is inversely proportional to the square root of the density (Graham's law). They can also be separated by condensing the less volatile constituents, or by contact with solids or liquids which absorb or combine with some constituents but not with others.

2. **Liquids** can be separated from insoluble solids by decantation or filtration. They can be separated from soluble substances which do not vaporise by means of

(*a*) ordinary distillation ;
(*b*) vacuum distillation ;
(*c*) steam distillation.

Mixtures of volatile liquids, or of liquids with volatile solids, can be separated from one another by fractional distillation ; in some cases, however, mixtures of *minimum boiling-point*, *e.g.*,

Alcohol = 95·59 per cent.
Water = 4·41 per cent.,

or mixtures of maximum boiling-point, *e.g.*,

Water = 79·76 per cent.,
Hydrogen chloride = 20·24 per cent.,

are obtained instead of pure substances. Liquids can also be purified by cooling them until they crystallise, and then draining off the liquid impurities.

3. **Solids** may be separated from non-volatile impurities by melting and distilling, or by sublimation. The commonest method of purification is, however, by dissolving the solid in a liquid solvent and separating the pure substance in the form of crystals by evaporating or by cooling the solution. In some cases a solid may be purified by liquation, *i.e.*, by heating the solid and draining off the more fusible impurities.

CHAPTER III

METHODS OF IDENTIFICATION AND TESTS OF PURITY

A.—The Law of Constant Properties.

Tests of Purity.

In the preceding chapter a description has been given of various methods by which raw materials, occurring naturally or manufactured in a crude condition, may be purified. It is necessary next to discuss the methods by which the purity of the product may be established.

Proust in 1806 pointed out that pure substances must possess :—

(1) Constant properties ;

(2) Constant composition, in the case of compound substances ; or freedom from foreign elements, in the case of simple substances.

Of these two statements, the LAW OF CONSTANT PROPERTIES is the more fundamental, since the second, known as the LAW OF CONSTANT COMPOSITION or the LAW OF FIXED PROPORTIONS, merely describes one of the many constant properties of a pure substance, namely, its constant composition.

The Law of Constant Properties.

The LAW OF CONSTANT PROPERTIES implies that the properties of a pure substance are independent of (*a*) its previous treatment, (*b*) its origin.

(*a*) Purification is usually accompanied by a gradual change of properties; but, when once the impurities have been got rid of, no further change should be produced by further purification. It often happens that one method of purification will remove certain impurities, but is unable to remove others. In such cases the change of properties may be arrested until new methods of purification are introduced ; but when two or three methods have been tried, and the properties of the product still remain constant, it is usually safe to assume that purification is substantially complete. Thus in the purification of alcohol by distillation, a product is obtained which still contains 4·41 per cent. of water ; it boils constantly at 78·13° under a pressure of 760 mm., and has a constant density 0·8195 gram per c.c. at 0°, and might easily be mistaken for a pure substance ; but when the pressure is altered the

mixture is resolved by further distillation into fractions having different compositions and different properties. After drying with quicklime, however, the liquid boils constantly at 78·39° under a pressure of 760 mm. and has a constant density of 0·80624 gram per c.c. at 0° ; these properties are not altered by further fractionation, either under high or under low pressure, and the product is therefore now substantially pure.

(*b*) When dealing with raw materials, it is often found that samples from different sources differ very widely from one another, both in their properties and in their market value ; but if the same product is finally extracted from them, it should have the same properties and the same value, from whatever source it may be derived. If, therefore, two samples of the product can still be recognised as coming from different sources, it is clear that the process of purification is still incomplete. Thus, in the case of ALCOHOL, the fact that different samples of spirit are known by different names (rum, gin, brandy, whiskey, etc.), and that several varieties or brands are distinguished and sold at different prices under each of these heads, is clear evidence that none of them is a single pure material or even a homogeneous mixture of alcohol and water. Alcohol which has been distilled in such a way as to free it from volatile oils cannot be recognised as belonging to any of the above groups, and is known as SILENT SPIRIT. It has been suggested that this name implies that the spirit is " silent as to its origin " ; if so, no better tribute could be paid to the purity of the product. Again, SUGAR is essentially the same material, whether it is prepared from the sugar-cane or from beetroot. In the early stages of purification there is a very wide difference between the " moist " sugar of the sugar-cane, often called Demerara sugar, and crude beet-sugar. Complete purification should remove all traces of the difference, and this condition is practically reached in the dry and colourless " granulated " or " lump " sugar. It is stated, however, that an expert can distinguish between the two kinds of sugar, and that the earthy character of the beetroot can be recognised by a slight odour when beet-sugar is boiled. This statement, supported as it is by a small difference in the market value of the two products, indicates that the sugar, although highly purified, is not yet pure.

Constant Properties in Gases, Liquids, and Solids.

In the case of gases and liquids, the Law of Constant Properties holds good without reservation. As soon as the physical conditions of temperature, pressure, etc., have become steady, the properties of a pure gas or liquid settle down to fixed and definite values. In the case of solids, however, it is possible to change the properties without changing the composition. Thus, samples of salt which are of equal purity may be obtained in crystals of different sizes according to the conditions under which they are crystallised. Again, it is well known

that the properties of copper, even when carefully purified, are altered profoundly by hammering or by drawing into wire. In these operations the copper increases in volume, loses much of its ductility, and becomes brittle, without suffering any change of composition, or the loss of any degree of purity. In such cases, in order to secure complete identity of properties, it is necessary to treat the two samples in a similar way before making tests of their properties. For instance, the two samples of salt should be crystallised in the same way, and the two samples of copper should be melted and cast under as nearly as possible the same conditions. By bringing the material into a liquid state, it is usually possible to eradicate all traces of its past history and to reduce it to a condition in which its properties depend exclusively on its composition and its degree of purity.

Qualitative and Quantitative Tests.

In many cases the appearance of a material affords a clue to its degree of purity. Crude materials are often coloured, and the colour may serve to indicate the extent to which they are contaminated by foreign substances. Water which is muddy or coloured or has a very pronounced taste is obviously not pure, since these characteristics disappear when the water is purified. Crude sea salt and rock salt alike reveal the presence of impurities by a coloration which disappears when the salt is recrystallised, the brilliant whiteness of the recrystallised salt being an essential property of the pure material. So also in the case of alcohol, the successive stages of purification are marked by the disappearance of colour and other features which reveal clearly the presence of impurities.

In scientific work these qualitative tests are of secondary importance and reliance is placed almost exclusively on properties which can be measured and expressed by means of numbers; but it is important not to underestimate the value or the delicacy of qualitative tests, especially in the recognition of traces of foreign substances in familiar products. Thus the impurities which distinguish beet-sugar from cane-sugar, or one brand of distilled spirit from another, are too minute to influence the physical properties of these substances, and could probably be detected in no other way than by their influence on the trained senses of taste and smell.

Identification by Means of Measurement.

Properties that can be measured and expressed by means of numbers are of great value, not only in testing the purity of a given sample, but also in writing out a description by means of which a pure substance may be recognised and identified. This method of identification is used in everyday life in the description of missing articles or persons, by giving the actual dimensions of the article or the height of the person; but it reaches its highest development in scientific work. Thus a liquid such as ether might be described as *volatile*, *inflammable*,

lighter than water, *not miscible with water*, but *miscible in all proportions with dry alcohol*, *colourless*, *mobile*, with a *characteristic odour*, and *not crystallisable* even by severe cold ; but these nine qualitative statements would not suffice to distinguish it from petrol or from scores of other liquids possessing similar properties. If, however, the density after purification is given as 0·7191 gram per c.c. at 15°, and the boiling-point as 34·6° under 760 mm. pressure, identification becomes a matter of almost absolute certainty. Moreover, whilst the recognition of the liquid by means of its characteristic odour cannot be transmitted or put on record, identification by means of numbers can be carried out by anyone who possesses the necessary standards of mass, volume, and temperature.

The certainty of this method of identification may be tested by trying to discover a liquid in which the density, boiling-point, and freezing-point of water are reproduced. The closest imitations of the properties of water are probably found in benzene, formic acid, formamide, and hydrazine, but in each case the divergence of properties is much greater than the maximum error of careful measurements, and absolute agreement in three different measurements is altogether exceptional.*

TABLE 1.—PHYSICAL PROPERTIES OF LIQUIDS.

	Water.	Benzene.	Formic Acid.	Form-amide.	Hydr-azine.
Freezing-point	0°	5·58°	8·6°	− 1°	1·4°
Boiling-point	100°	80·2°	100·7°	194°	113·5°
Density	0·99823 at 20°	0·8736 at 20°	1·2256 at 15·1°	1·337 at 14·1°	1·0114 at 15°

The properties used for identification must be such as can be measured easily and correctly, since a doubt will often arise as to whether a small difference in the numerical value of a property is due to a real difference in the materials, or merely to experimental errors. It is also important that the measurements shall be easily reproducible, so that different workers may make use of the same standards. The properties that are used most frequently are set out below.

B.—MEASUREMENTS OF DENSITY.

Definitions of Density.

The density of a substance is measured by the mass which occupies unit volume. It is therefore expressed in grams per cubic centimetre,

* It actually occurs, however, in certain "enantiomorphous" compounds, which are related to one another as a right hand is related to the corresponding left hand, and which differ only in those properties in which right-handedness and left-handedness are possible. "Isotopic elements" which are substantially identical in all properties but atomic weight are described in chapters XXXI and XLV.

or, in the case of gases, in grams per litre ; more rarely, in pounds per cubic foot or pounds per gallon. As nearly all substances expand when heated, the density must be measured at a definite temperature. This precaution is most important in the case of gases, and least important

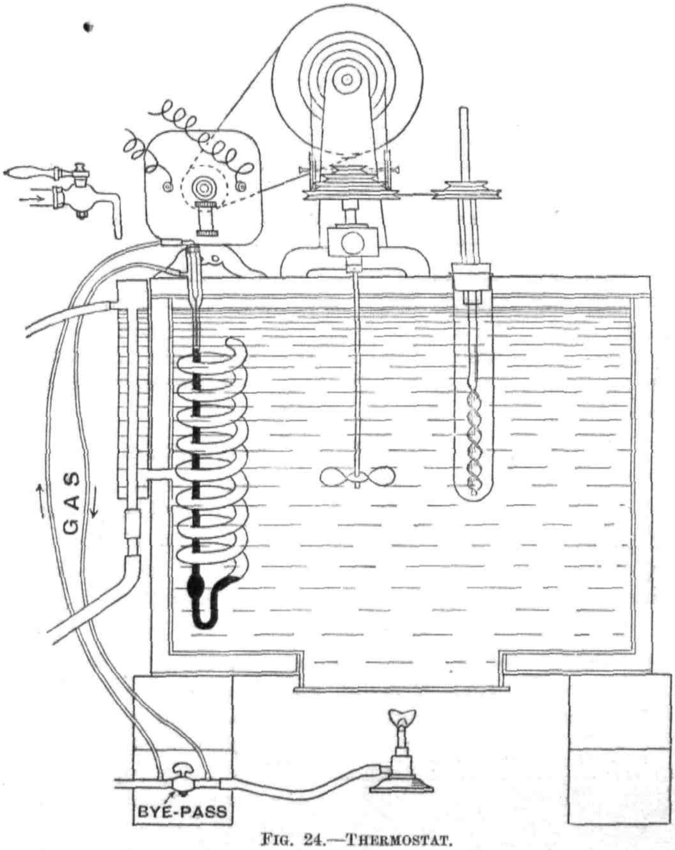


FIG. 24.—THERMOSTAT.

A constant temperature is maintained in a well-stirred bath of water by means of the spiral gas-regulator, shown on the left-hand side of the bath. If the temperature should rise, the toluene with which the spiral is filled expands, and drives up a column of mercury in the vertical tube of the regulator. This closes the capillary through which the main supply of gas passes to the burner, the flame being kept alight by means of a bye-pass. When the temperature falls the mercury recedes from the capillary and the burner again receives a normal supply of gas. In a well-stirred bath the temperature of the water can be maintained without difficulty at 20° ± 0·01°.

in the case of solids. A THERMOSTAT for maintaining a constant temperature in a bath of water is shown in Fig. 24. Pressure, which greatly affects the density of a gas, has so little effect upon the density of a liquid or solid that its influence is usually neglected.

An alternative method of expressing the density of a substance is by comparing it with a standard substance. Thus, the density of a gas is often measured relatively to that of air or hydrogen ; this method has the advantage of eliminating most of the variations due to changes of temperature and pressure. Liquids and solids are compared with water. The ratio of the two densities is known as the RELATIVE DENSITY, although the misleading term "specific gravity" is also employed sometimes. When this method of measurement is used, it is necessary to specify the temperature of the standard material as well as that of the substance that is being measured ; relative densities are therefore given for temperatures such as 15°/15°, or 15°/4°. The choice of water at 4° as a standard of relative densities has the advantage that at this temperature the density of water is almost exactly 1 gram per c.c., so that the relative density is numerically equal to the absolute density in grams per cubic centimetre ; in the present volume, *all densities for which other units are not given are expressed in terms of this unit, i.e.*, in grams per cubic centimetre.

The Density of Liquids.

The density of a liquid is measured by comparing the weights of the given liquid and of water that are required to fill the same vessel. Tables have been prepared which give the absolute densities of water at different temperatures with a high degree of accuracy. These can be used to calculate the capacity of the vessel from the weight of water which it contains ; or the relative density may be multiplied by the density of water in order to convert it directly into an absolute density.

In accurate measurements of density allowance must be made for the buoyancy of the air, which produces marked alterations in the apparent weight of a substance. Taking the density of air as 1·2 grams per litre, the weight of a kilogram of water would be diminished to 998·8 grams by the displacement of 1·2 grams of air ; but the brass weights, which displace about one-eighth of this volume of air, would also be reduced in weight by about one-eighth of this amount : the actual loss in the apparent weight of the water is therefore about 1·06 grams per kilogram. This correction decreases as the density increases, and is of opposite sign in the case of substances more dense than the brass weights. The buoyancy of the air usually affects the third decimal place in the density ; but its influence is much less when the relative density is being determined of two liquids such as water and alcohol, or water and an aqueous solution which do not differ very widely in density from one another. In measuring densities to four decimals an average value for the density of the air may be used : beyond this, it is usually necessary to calculate a special value from the observed temperature and pressure of the air.

The Design of Pyknometers.

The vessels used for measuring the relative densities of liquids are known as PYKNOMETERS. The essential features of a good pyknometer are as follows :—

(*a*) *Its capacity must be fixed so that the volume of liquid that is required to fill it is always exactly the same.* A bottle with a wide neck is unsuitable for a pyknometer, since the level in the neck would not be altered perceptibly by the addition or removal of a few drops of the liquid ; on the other hand, a stoppered bottle, with a narrow groove cut in the stopper to allow the excess of liquid to escape, makes a very good pyknometer, because a small fraction of a drop is sufficient to raise the level of the liquid from the bottom to the top of the groove. The volume of liquid in a pyknometer is usually fixed by adjusting it to a mark on a narrow capillary tube, as in the pyknometer shown in Fig. 25. This is provided with two capillary tubes for convenience of filling, and is specially shaped so that bubbles of air are not retained at the top of the bulb when the pyknometer is tilted in order to fill it from a beaker. The upper capillary opens out into a tube into which the liquid may expand when its volume has been adjusted at a temperature below that of the atmosphere ; this tube is better than a bulb, as it can be wiped dry with filter-paper ; evaporation of the liquid may be checked by slipping a glass cap over the end of the tube. In the pyknometer of Johnson and Adams (Fig. 26), a still more accurate adjustment of volume is obtained by the contact of two carefully worked glass surfaces.

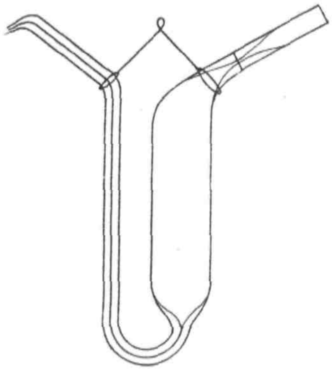


FIG. 25.—PYKNOMETER FOR MEASURING DENSITY OF LIQUIDS.

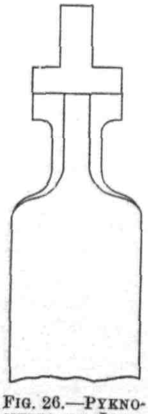


FIG. 26.—PYKNOMETER OF JOHNSON AND ADAMS (upper part only).

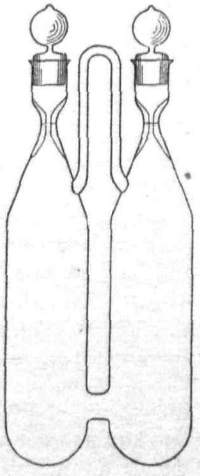


FIG. 27.—BOUSFIELD'S PYKNOMETER.

(*b*) *The form of the pyknometer should allow of a rapid adjustment of the temperature of the contents.* From this point of view, a bottle or

a spherical bulb compares unfavourably with the tube shown in Fig. 25. On the other hand, the use of a wide bulb has the advantage of reducing the weight of glass required to enclose a given weight of liquid and of diminishing the area of the surface on which dirt and moisture may collect. When, therefore, a good thermostat and ample time are available for measurements of great accuracy, a stout bulb is often employed, as in the pyknometers used by Bousfield for measuring the densities of aqueous solutions to six places of decimals (Fig. 27) and by Wade and Merriman for measuring the density of volatile liquids such as alcohol at the temperature of melting ice (Fig. 28).

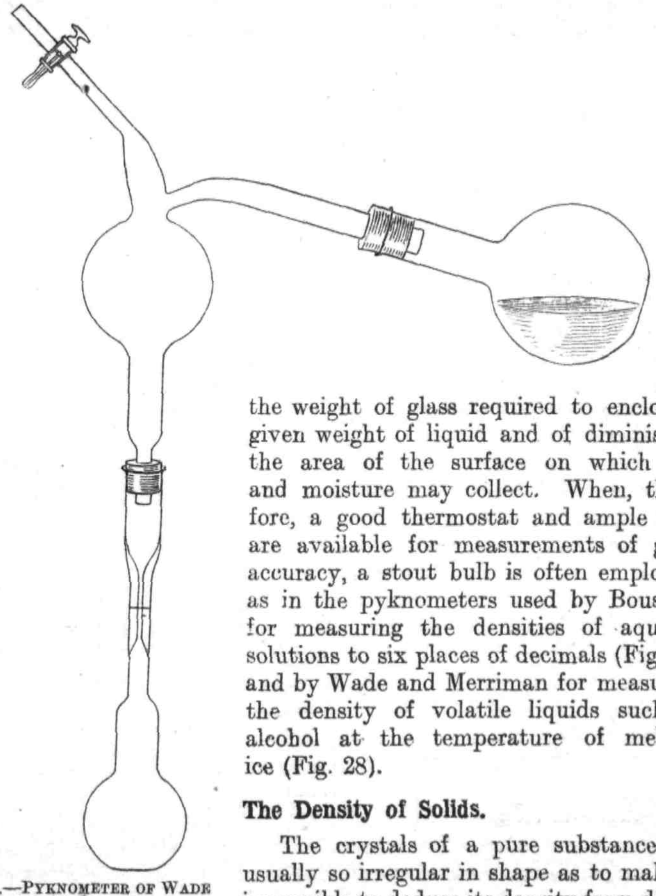


FIG. 28.—PYKNOMETER OF WADE AND MERRIMAN.

By means of the apparatus shown in the upper part of the figure the air can be exhausted by means of a vacuum pump from the pyknometer and from the liquid, before this is transferred from the flask to the pyknometer. This method is suitable for pure liquids, but not for solutions, the composition of which might be altered by evaporation.

The Density of Solids.

The crystals of a pure substance are usually so irregular in shape as to make it impossible to deduce its density from direct measurements of weight and volume; the densities are therefore determined either by DISPLACEMENT of a liquid or by FLOTATION in a liquid of equal density.

(*a*) *Density of solids by displacement.*—A liquid must be chosen in which the solid does not dissolve; thus, water may be used for many organic compounds, whilst paraffin is a suitable liquid for common salt. The weight of liquid required to fill a wide-necked pyknometer is determined accurately. A known weight of solid is intro-

duced into the pyknometer and the weight is determined again after filling up with the liquid. In this way the weight of solid is found which displaces a known weight of liquid, and the ratio of the two weights gives the relative density of solid and liquid. Great care is needed to remove all the air-bubbles which adhere to the solid; in accurate work, the pyknometer is exhausted with a good vacuum pump after introducing the solid, and the liquid is introduced from a filler similar to that shown in Fig. 28. The pyknometer (Fig. 26) designed by Johnson and Adams for accurate measurements of the small changes of density which occur when metallic wires are annealed is very suitable for work of this kind.

(*b*) *Density of solids by flotation.*—The solid is placed in a glass vessel and covered with a liquid in which it does not float. A second liquid of greater density is added until the last particles of solid just begin to rise in the mixture. The density of the mixture, which is exactly equal to that of the solid, is then determined in the usual way. Air-bubbles, or mother-liquor included in the crystals, do not affect this method of measurement, as they merely cause a few particles to rise prematurely to the surface. Moreover, the quantity of solid that is required is very small, a single crystal crushed into coarse powder being quite sufficient. The method is, however, limited by the necessity of finding liquids dense enough to produce flotation. The liquids most commonly used are as follows :—

TABLE 2.—LIQUIDS FOR FLOTATION OF SOLIDS.

Light liquid.	*Density.*	*Dense liquid.*	*Density.*
Water . .	1	Saturated solution of sodium borotungstate	3·02
Water . .	1	Saturated solution of barium mercury iodide	3·58
Methyl alcohol	0·81	Methylene iodide	3·28

Easily melted salts, such as mercurous thallous nitrate, melting-point 76°, density 5·3, may also be used for experiments on flotation, but not at atmospheric temperatures. Heavier liquids (such as metallic mercury) are known, but they cannot be used in the absence of a suitable diluent; even if this difficulty could be overcome, the opacity of the mercury would still render it unsuitable for this purpose. In practice, therefore, the method of flotation is usually limited to solids of density below about 3·5.

The Density of Gases and Vapours.

The densities of gases and of vapours are of great importance as a means of determining the relative weights of gaseous molecules

(Chapter XIII). Accurate measurements are, however, very difficult to make. Not only are the densities extremely sensitive to small variations of temperature and pressure, but their magnitudes are so small that very large volumes must be taken in order to provide a reasonable quantity for weighing.

(*a*) *Gases.*—In general, the density of a gas is determined by weighing a large glass globe, first vacuous, and then filled with the gas at a known temperature and pressure. Increased accuracy is secured by using a sealed counterpoise of about the same weight and volume as the bulb used to contain the gas (Fig. 48, p. 90): this serves to eliminate many of the errors caused by fluctuations in the buoyancy of the air, or by variations in the amount of moisture which it contains. The special conditions used in the most accurate measurements of the densities of oxygen and hydrogen are set out on pp. 90 and 91; modern devices for weighing gases condensed on charcoal are described on p. 408.

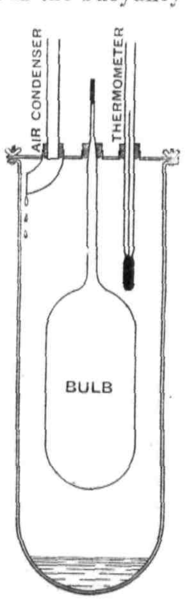


FIG. 29.—APPARATUS FOR VAPOUR DENSITY (Dumas' method).

(*b*) *Vapours.*—The densities of vapours may be determined by three principal methods.

(i) In DUMAS' METHOD the weight is determined of the vapour which fills a bulb of known volume at a measured temperature and pressure.

A modern form of Dumas' apparatus is shown in Fig. 29. The bulb, containing a few drops of liquid, is heated in the vapour of a liquid of higher boiling-point, until all the air has been driven out and vapour no longer escapes from it; the tip is then heated to drive off condensed liquid and sealed. When cold, the bulb is weighed against a sealed counterpoise and the gain or loss determined as compared with the original weight when filled with air. The tip of the bulb is then broken under water, when the volume of water drawn in is equal to the volume of air displaced by the vapour. The temperature and pressure are read (i) at t° and p mm. when the bulb is weighed full of air and (ii) at t' and p' when it is sealed up filled with vapour. The weight of air originally filling the bulb is calculated from the formula

$$w = v \times 1{\cdot}2 \times \frac{p}{760} \times \frac{273}{273 + t} \quad . \quad . \quad . \quad . \quad \text{(i)}$$

where w is the weight in grams and v is the volume of air in litres at t° and p mm. pressure; the gain or loss of weight during the experiment then gives the weight of the vapour filling the bulb at a known temperature t' and pressure p'. If desired this can be compared with the weight of an equal volume of hydrogen calculated from the formula

$$w' = v \times 0{\cdot}09 \times \frac{p'}{760} \times \frac{273}{273 + t'} \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

(ii) In HOFMANN'S METHOD (Fig. 30A) a known weight of liquid in a tiny bulb, C, is allowed to evaporate at the top of a barometer heated by a vapour jacket. In this way the volume of a known weight of vapour is determined at a known temperature and under a pressure given by the difference between the normal barometric height and the observed column *a b*.

(iii) In VICTOR MEYER'S METHOD the vapour from a known weight of liquid displaces its own volume of air, which is collected and measured at the atmospheric temperature.

The large bulb, *b*, Fig. 30B, is heated in a vapour jacket, *c*, until no more air is expelled; a tiny bottle, C, containing a known weight of liquid is then dropped into the bulb, the rubber stopper, *d*, being removed for this purpose and quickly replaced. The air displaced through the side-tube, *a*, is collected at *g*, and its weight calculated from the formula (i) above.* In this method the temperature of the bulb need not be known; it is therefore possible to work with a bulb of porcelain or silica heated to a constant but unknown temperature in a muffle furnace. In calculating the vapour density, the weight of gas displaced by the vapour can be calculated as if hydrogen had been used instead of air, and the vapour density deduced relatively to hydrogen.

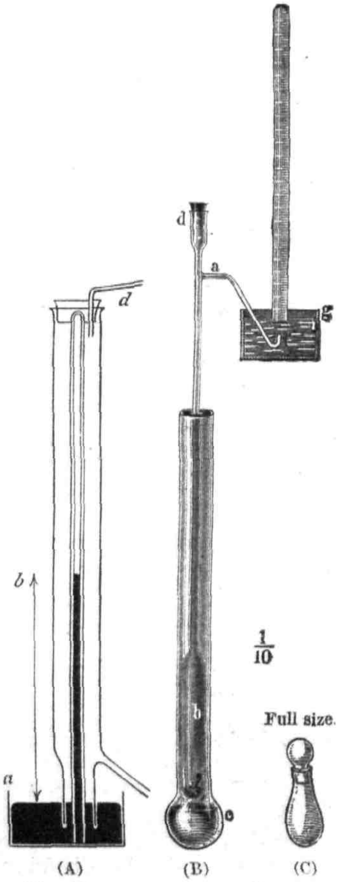


FIG. 30.—APPARATUS FOR VAPOUR DENSITY.
A, Hofmann's method; B, Victor Meyer's method; C, bulb for liquid.

C.—BOILING-POINTS.

Boiling-points and Freezing-points.

It is a general characteristic of pure substances that the temperature remains constant during the whole of the time that the substance is being melted or distilled. This constancy of the melting-point or boiling-point is one of the best criteria of completed purification. It is also used in thermometry to provide "fixed-points" for the scale of temperatures. Thus in the Fahrenheit system the freezing-point and boiling-point

* When reading the volume of air the water must be at the same level inside and outside the graduated tube, and the vapour-pressure of water must be deducted from the barometric pressure of the air.

of pure water are taken by definition as 32° F. and 212° F. In the Centigrade scale they are taken as 0° C. and 100° C ; this scale is used throughout this book, usually without the distinguishing letter "C." Boiling-points and freezing-points are also used as secondary standards for calibrating thermometers and pyrometers at temperatures far removed from these two fixed points. The principal data used for this purpose are as follows :—

TABLE 3.—BOILING-POINTS AND FREEZING-POINTS.

Boiling-points. (under a pressure of 760 mm. of mercury).		*Freezing-points.*	
Hydrogen	− 253°	Mercury	− 38·9°
Oxygen	− 183·0°	**Water**	**0°**
Carbon dioxide (temperature of sublimation when mixed with an inert liquid)	− 78·5°	Tin	+ 231·9°
Water	**+ 100°**	Cadmium	+ 320·9°
Naphthalene	+ 217·96°	Lead	+ 327·4°
Benzophenone	+ 305·9°	Zinc	+ 419·4°
Sulphur	+ 444·6°	Antimony	+ 630·0°
		Aluminium	+ 658·7°
		Common salt	+ 801°
		Silver	+ 960·5°
		Gold	+1063·0°
		Copper	+1083·0°
		Nickel	+1452°
		Iron	+1530°
		Palladium	+1549°
		Platinum	+1755 ± 5°

In all measurements of temperature it is assumed that the thermometer is immersed completely in the medium of which the temperature is to be recorded. If any part of the mercury remains outside, a correction is necessary for the portion of the stem which remains exposed. The correction δT is given by the formula

$$\delta T = \frac{n}{6300}(T - T_0),$$

where n is the number of degrees covered by the exposed thread of mercury, T is the temperature recorded, and T_0 is the temperature of the exposed stem as recorded by a small auxiliary thermometer. Thus, if the stem is exposed beyond the 100° graduation and is at a temperature of 20°, the corrections are: 0 at 100°, + 1·0° at 150°, + 2·8° at 200°, and + 5·5° at 250°.

Influence of Pressure.

In measuring boiling-points it is necessary to pay attention to the pressure. In the case of water the boiling-point under the standard pressure of 760 mm. of mercury is by definition exactly 100°. The variation of the boiling-point with pressure is shown in the following table :—

730 mm.	98·877°	760 mm.	100·000°
740 mm.	99·255°	770 mm.	100·366°
750 mm.	99·630°	780 mm.	100·728°

Other liquids show similar variations, but the magnitude of these must be determined experimentally for each liquid.

In stating the pressure under which a liquid boils at a given "boiling-point," it is not sufficient merely to record the height of the barometric column. This must be corrected for the influence on the density of the mercury and on the length of the barometer-scale of a rise of temperature from 0° to the prevailing temperature of the atmosphere: further corrections are needed to allow for the diminution of the force of gravity if the barometer is substantially above sea-level, and for its increase if the latitude is greater than 45° north or south of the equator. In a typical case the corrections work out as follows:—

Boiling-point of acetic acid	118·11 to 118·13°
Correction for thermometer error	− 0·05°
Correction for exposed stem of thermometer .	+ 0·04°
Corrected mean temperature . . .	118·11°
Barometer reading	768·2 mm.
Correction for temperature of mercury (20°)	− 2·62 mm.
Correction for height above sea-level (200 ft.)	− 0·01
Correction for latitude (51° N.)	+ 0·41
Corrected pressure	766·0 mm.

Rise of boiling-point per mm. = 0·038°, rise for 6 mm. = 0·228°.
Normal boiling-point under 760 mm. pressure = 118·11° − 0·228° = **117·88°**.

When only small quantities of liquid are available there is considerable risk of SUPERHEATING, *i.e.*, of heating the material above its true BOILING-POINT, namely, the temperature at which liquid and vapour are in equilibrium with one another. A *liquid* may be superheated slightly, since vapour is not always produced when the boiling-point is reached, especially when the liquid is free from air and is heated directly by a flame. A *vapour*, on the other hand, may be superheated to any extent as soon as it has been separated from the liquid; the invisible DRY STEAM readily cools, however, and becomes "wet" with visible droplets of liquid, and it is in the WET STEAM that the boiling-point can be observed most easily and accurately.

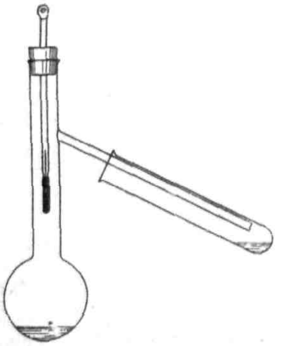


FIG. 31.—APPARATUS FOR DETERMINING BOILING-POINTS.

A simple apparatus for determining the boiling-point of a liquid is shown in Fig. 31. The liquid is distilled from a small distilling flask into a test-tube, with a very small flame; its temperature is recorded by means of a short thermometer, the thread of which is surrounded completely (if possible) by the vapour; the bulb of the thermometer is wrapped in cotton wool and, as this becomes wetted with condensed liquid, superheating can be prevented completely and the boiling-point determined accurately, even with a very small quantity of liquid.

The boiling-point of a solution is usually higher than that of the pure liquid condensed from the vapour, and must therefore be determined in the liquid. The special precautions needed to prevent superheating are described in Chapter XVI, p. 173.

Methods of Measurement.

The most accurate method of determining the boiling-point of a liquid is to distil a large quantity of it through an efficient still-head, to notice the temperature of the vapour as distillation proceeds, and to collect separately a large middle-fraction boiling at a constant temperature which may be recorded as the boiling-point of the sample.

D.—FREEZING-POINTS.

Freezing-points and Melting-points.

The temperature at which a liquid freezes or a solid melts is even more valuable than the boiling-point as a means of identifying a substance and testing its purity. When proper precautions are taken, the melting-point of a solid and the freezing-point of the liquid are identical, since in each case the temperature is controlled by the equilibrium between solid and liquid. Any attempt to raise the temperature of the liquid is therefore followed by the melting of a further quantity of the solid and the restoration of the liquid to its former temperature; conversely, any attempt to cool the mixture will be followed by the freezing of a further quantity of liquid until the balance of temperature has been restored again.

Experimental Methods.

(*a*) In order to determine the correct melting-point or freezing-point of a substance, the liquid and solid must be brought into intimate contact, since it is only in this way that OVERHEATING and UNDERCOOLING can be prevented. The best method is to cool the liquid a little below its normal freezing-point, and then to start crystallisation throughout the liquid by stirring vigorously; as crystals separate. the temperature rises to a maximum at the true freezing-point or melting-point of the substance, and may remain steady within a few thousandths of a degree at this temperature for some minutes. This method can also be applied to solutions, provided that the cooling is slow and the overcooling slight, so that only a small quantity of crystals separate.

The progressive purification of a sample of about two litres of acetic acid is shown in the following table, where the INITIAL FREEZING-POINT of the sample was determined as described in the preceding paragraph, whilst the "final freezing-point" was observed (when nearly all the acid had been frozen and only about 100 to 200 c.c. remained unfrozen in a central cavity) by breaking through the ice and inserting the thermometer into the mother-liquor. This was then poured away, the acid melted, and the whole process

repeated. The complete purification of the acid was shown (i) by the constancy of the "initial freezing-point," and (ii) by the close approach to the initial freezing-point of the "final freezing-point" of the least pure portion of the acid.

Initial freezing-point .	16·31°	16·45°	16·55°	16·58°	16·59°	16·595°	16·60°
Final freezing-point .	15·98°	16·07°	—	16·49°	16·49°	16·54°	16·56°

The freezing-point of the pure acid may be taken as **16·60 ± 0·01**°.

(*b*) The melting-point of a small quantity of a substance may be determined by freezing a few drops round the bulb of a small thermometer and observing the steady temperature as the solid melts away. By this method the melting-point of ice may be determined correctly without using more than a single cubic centimetre of water. Melting-points, as distinguished from freezing-points, may also be determined with even smaller quantities by using the apparatus shown in Fig. 32.

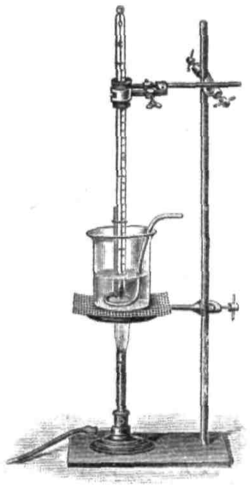


FIG. 32.—APPARATUS FOR DETERMINING MELTING-POINTS.

A small crystal of the solid is crushed and the powder transferred to a tube about a millimetre in diameter, made by drawing out a test-tube. This tube is attached by means of a rubber band (or merely by wetting it) to a thermometer, which is heated in a small beaker containing water, sulphuric acid, or molten paraffin wax. When the solid melts, the reading of the thermometer is taken: slow heating and vigorous stirring are needed to secure accurate values for the melting-point.

(*c*) Impure materials change in temperature during freezing or melting, even when precautions are taken to bring the liquid and solid intimately into contact. Sea-water, for instance, not only freezes at a lower temperature than distilled water, but as ice is frozen out from it the freezing-temperature falls lower and lower. So, also, an impure solid, when heated gradually, does not melt sharply at a constant temperature, but gradually "sinters," *i.e.*, becomes softened and sinks down slowly, so that the melting may be spread over a range of several degrees.

(*d*) In some cases the liquefaction of a solid may be due to decomposition; the decomposition-temperature, although less sharp than a melting-point, is often of value in identifying a substance.

E.—OTHER PROPERTIES.

Solubility.

Substances such as common salt may be characterised by measuring their solubility in water or in some other liquid. By determining the

density as well as the concentration of the saturated solution a second independent constant may be obtained. As the solubility varies greatly with temperature, the measurements must be made under definite conditions, *e.g.* at 20°. Better results are obtained by preparing a saturated solution and determining its composition than by attempting to measure directly the amount of salt required to saturate a known quantity of liquid, or the quantity of liquid required to dissolve a known quantity of the solid.

An efficient apparatus for preparing saturated solutions is shown on the right in Fig. 24, p. 32. The tube in which solid and liquid are brought into contact is provided with a stirrer driven from a motor, so that it can be run for any length of time that may be necessary to secure saturation. In the case of a fine powder, which can be churned up throughout the liquid, a few minutes will suffice; but a coarse, heavy powder may require an hour or more. The temperature of the liquid is kept constant by immersing the tube in a well-stirred thermostat controlled by an automatic gas-regulator.

Electrical Conductivity.

In the special case of water, the best test of purity is to measure its electrical conductivity. This diminishes as the water is purified, and in very pure water disappears almost completely. The electrical resistance and the conductivity of various samples of water are shown in the following table:—

TABLE 4.—ELECTRICAL CONDUCTIVITY OF WATER.

	Specific resistance.	*Specific conductivity.*
Sea-water (about)	1,000 *ohms*	0·001 *mhos*
River-water (about) . . .	10,000	0·000,1
Ordinary distilled water . .	100,000	0·000,010
Water distilled fractionally . .	1,000,000	0·000,001
Water distilled fractionally in a current of purified air . .	5,000,000	0·000,000,2
Redistilled after storing for five years in a vacuum and in contact with platinum	25,000,000	0·000,000,04

Optical Properties.

Transparent minerals and gems may be identified by their power of refracting light as expressed by measurements of the REFRACTIVE INDEX. In the case of oils and fats, both the REFRACTION and DISPERSION are used. Many natural organic compounds possess the power of rotating the plane in which the vibrations of a beam of polarised light are taking place: measurements of their OPTICAL ROTATORY POWER and of their ROTATORY DISPERSION are then important for identifying and estimating them; in the case of ENANTIOMORPHOUS

substances (see footnote, p. 31), this is almost the only physical property that can be used for this purpose.

Chemical Properties.

Ordinary chemical tests are described in subsequent chapters of this book, but reference may be made here to chemical inactivity as a supreme test of purity. Many of the commonest chemical changes can be stopped altogether by purifying materials which usually interact with great readiness. This can only be done by employing the utmost care in purification, which must be carried far beyond the point at which the impurities are able to influence the ordinary physical properties of the materials. A fuller account of some of these phenomena is given below (pp. 244 and 259).

SUMMARY AND SUPPLEMENT.

1. Pure materials may be recognised by the fact that they have (*a*) constant properties, (*b*) constant composition.

2. Under constant physical conditions, the properties of a pure substance, if gaseous or liquid, should be independent of (*a*) its previous treatment, (*b*) its origin; certain properties of solids are influenced by previous treatment, but these effects can be eliminated, *e.g.*, by fusion or by dissolution in a solvent.

3. The properties most frequently used to identify pure materials and to test their purity are (*a*) density, (*b*) boiling-point, (*c*) freezing-point, (*d*) solubility, (*e*) electrical conductivity, (*f*) optical properties such as refraction, dispersion, and optical rotatory power. In addition, qualitative tests such as colour, taste, and smell are often of very great value as methods of identification and as tests of purity.

CHAPTER IV

SALTS, ALKALIES, AND ACIDS.

Mercury, Sulphur and Salt.

Amongst the materials which have been studied by chemists three groups stand out as of predominant importance, namely,

(i) SALTS, with the ALKALIES and ACIDS which are closely related to them;

(ii) METALS, their ores, and the calces that are formed when the metals are burnt;

(iii) COMBUSTIBLE SUBSTANCES, such as charcoal, sulphur, and phosphorus, together with the products of their combustion.

In the alchemistic period, Aristotle's four ELEMENTS, *earth*, *air*, *fire*, and *water*, were replaced by the three PRINCIPLES, *mercury*, *sulphur*, and *salt*, corresponding with the three chief groups of substances, the metallic, the combustible, and the saline. It was from the study of these groups of substances that a knowledge of chemical composition was first derived. They also provided the material for the earliest studies of chemical affinity and of the conditions under which chemical changes take place. Definite knowledge on these subjects was acquired first in the case of the salts, as described in the present chapter. Experiments on metals and on combustible substances are described in chapters V, VII, VIII, and IX.

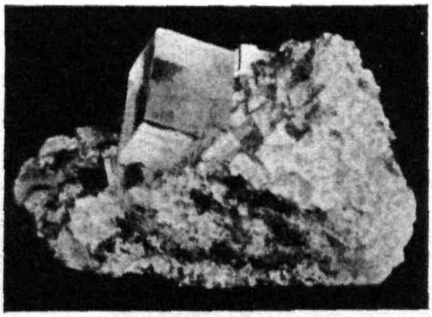


FIG. 33.—CRYSTAL OF ROCK SALT.

A.—SOLUBLE SALTS.

Common Salt as a Type.

One of the first substances to be prepared and purified in early times was COMMON SALT, obtained by evaporating sea-water in shallow pools on the sea-shore. The same substance is also mined as a mineral under the name of ROCK SALT (Fig. 33). Common salt (like rock-crystal, Fig. 11, p. 12) gave its name to a large number of substances which were described as SALTS. Thus, Boyle in 1680 defined a "salt" as "easily soluble in water" and possessing "a savour, whether good or evil."

Subsequently, the name was extended further to include substances of similar composition, even though these were not soluble in water, and had no characteristic taste.

Saltpetre and Sal-ammoniac.

(*a*) SALTPETRE OR NITRE is a colourless salt-like substance, formed by the decay of animal matter and found as an incrustation on the

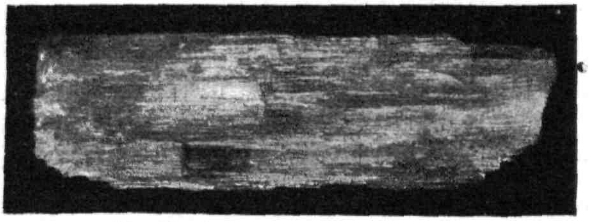


FIG. 34.—CRYSTAL OF SAL-AMMONIAC.

surface of the soil in the neighbourhood of stables, etc. It was introduced into Europe from the East, but was also manufactured in Europe to provide a supply of saltpetre for the making of gunpowder. Throughout the Middle Ages this salt was prepared in "nitre beds" containing lime and potash, on to which stable-refuse was constantly poured. At the present time it is also prepared artificially (p. 597), although large quantities are still imported from Bengal and other parts of India.

(*b*) SAL-AMMONIAC (Fig. 34), a second salt of animal origin, was manufactured by heating camels' dung. It differed from other salt-like substances in that it could be vaporised completely by gentle heat.

Alum, Green Vitriol, and Blue Vitriol.

ALUM (Fig. 8, p. 11), a beautifully crystallised salt with an astringent taste, has been known from classical times. It was prepared by

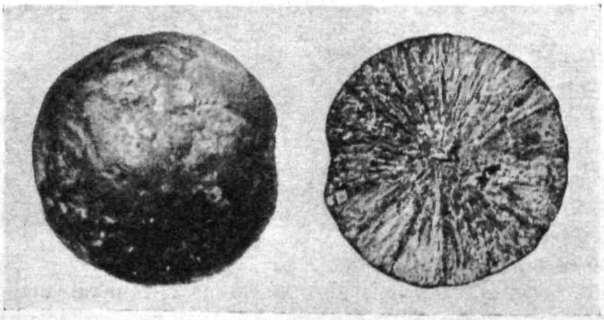


FIG. 35.—NODULE OF MARCASITE.

roasting ALUM-SHALE (a mixture of clay and coal containing iron pyrites) and extracting the mass with water. GREEN VITRIOL, as its

name implies, is a green, glassy salt (Latin, *vitrum*, glass). It was prepared by collecting MARCASITE (Fig. 35) or IRON PYRITES (Fig. 36),

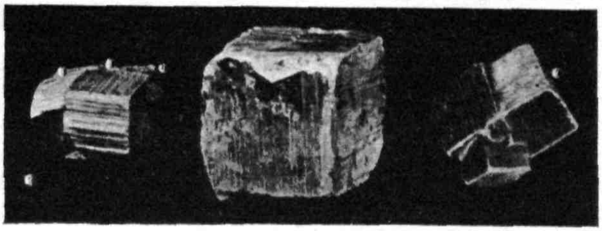


FIG. 36.—CRYSTALS OF IRON PYRITES.

breaking it up into powder, and allowing it to decay in contact with air and water. The mass was then extracted with rain-water, which was filtered and evaporated until crystallisation took place. The preparation of alum and of green vitriol was of great importance in the history of chemistry because it led directly to the discovery of the mineral acids. In the Middle Ages the word "vitriol" became synonymous with "crystal," but afterwards the term was restricted to substances similar in composition to green vitriol. The most important of these was BLUE VITRIOL (Fig 37), a deep-blue salt prepared by the weathering of copper pyrites, just as green vitriol was prepared from iron pyrites.

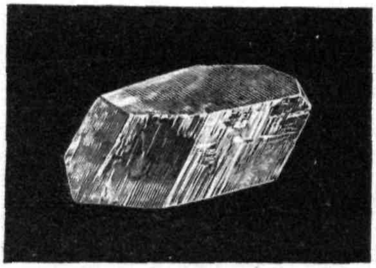


FIG. 37.—CRYSTAL OF BLUE VITRIOL.

Soda and Potash. The Alkalies.

The crystalline salt known as SODA was discovered at a very early period as a natural deposit on the shores of the "soda lakes" of Egypt. It was used as a cleansing agent under the name of "nitre" (Jer., ii, 22) a thousand years before soap was manufactured in Europe. The soda lakes are still being worked by an Egyptian company and continue to yield several hundreds of tons of soda per annum. Lake Magadi in East Africa is said to contain 200,000,000 tons of natural soda.

A white solid, closely resembling soda in many of its properties, was prepared by extracting the white ash of burnt wood with water in earthenware pots. It was known as POTASH (originally "pot-ash") or "pearl-ashes." During the Middle Ages, until the time of Boyle, potash was the only alkali used in Europe; afterwards, however, soda

was prepared from the ash of seaweeds and was used on a large scale, under the name of "barilla," for the manufacture of soap. These two substances, which effervesced when acids were poured upon them (Prov. xxv, 20), were distinguished as ALKALIES. By boiling them with lime they were converted, at the very beginning of the alchemistic period, into CAUSTIC ALKALIES; the effervescing alkalies were then distinguished as MILD ALKALIES.

A third alkali was prepared by heating sal-ammoniac with mild soda or potash. Like sal-ammoniac, it was readily vaporised by heat; but it resembled soda and potash in that it effervesced with acids. It was described as the "volatile alkali" in order to distinguish it from the non-volatile or "fixed alkalies" and was commonly known as SAL VOLATILE.

B.—ACIDS.

Vegetable Acids. Vinegar and Acetic Acid.

The first ACIDS to be discovered were of vegetable origin. No distinction was made between the acids of sour wine (acetic acid), sour grapes (tartaric acid), sour apples (malic acid), and lemons (citric acid); but sour wine, or VINEGAR, was for a long time regarded as the typical acid. The alchemists frequently used distilled vinegar and were able to some extent to concentrate the ACETIC ACID which it contains.

Properties of Acids.

The characteristic properties of vinegar were:

(i) its sour taste (Lat. *acetum*, vinegar; *acidus*, sour).

(ii) its action on the mild alkalies, soda and potash, which effervesced under the action of the acid.

(iii) its power of dissolving chalk (referred to by Livy), with effervescence.

(iv) its power of corroding metals, *e.g.*, of converting copper into VERDIGRIS.

At a later date, about the time of Boyle, acids were found to possess the power of changing the colour of vegetable extracts, especially syrup of violets, which changed from violet to green; litmus and the extract of blue cornflowers were changed from blue to red. Substances such as these, which are particularly sensitive to the action of acids, are used as INDICATORS for the detection of acids.

Mineral Acids. Oil of Vitriol or Sulphuric Acid.

A great advance was made in the discovery of a series of powerful MINERAL ACIDS. The first of these was OIL OF VITRIOL, a thick, heavy liquid first prepared by distilling either alum or green vitriol. It was prepared afterwards from sulphur, and has been known since 1787 as SULPHURIC ACID. The strong acid prepared from green vitriol is extremely corrosive; it chars wood and may even ignite turpentine or

spirits of wine. When poured into water it hisses violently and causes the water to boil. This strong acid was formerly known as NORDHAUSEN OIL OF VITRIOL, from the town in Germany where it was manufactured.

The acid is no longer corrosive when dilute, but has a very sour taste, acts vigorously on the alkalies and on chalk, and dissolves iron and tin, liberating an inflammable gas (Chapter VIII). The concentrated acid will also dissolve lead (in small quantities), copper, mercury, and silver, but gold is not attacked by it. It should be noticed that when oil of vitriol acts on chalk, most of the product is left undissolved as a sparingly soluble powder identical with the GYPSUM (Fig. 38) from which PLASTER OF PARIS is prepared.

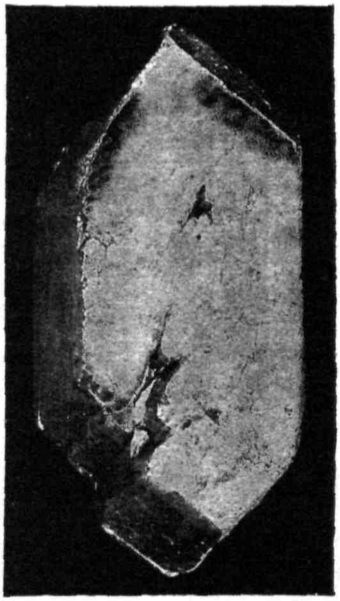


FIG. 38.—LARGE CRYSTAL OF GYPSUM OR SELENITE.

Aqua fortis, or Nitric Acid.

When a mixture of oil of vitriol and nitre is heated gently, a watery liquid distils which is known as AQUA FORTIS, or NITRIC ACID. The strong acid is quite as corrosive as oil of vitriol, but can be rendered harmless by diluting it with much water. It acts vigorously on the alkalies and dissolves chalk. Even when diluted with water it dissolves not only tin and iron, but also lead, copper, mercury, and silver. Gold is not attacked by nitric acid alone, but is readily dissolved by nitric acid to which sal-ammoniac, common salt, or spirit of salt (see below) has been added; the mixed acid which thus possesses the power of dissolving gold is known as AQUA REGIA.

Spirit of Salt.

When oil of vitriol acts on rock-salt a white, fuming gas is set free which was described as SPIRIT OF SALT. This does not condense spontaneously, but it may be collected by bringing it into contact with water. The acid thus produced was called MURIATIC ACID (Lat. *murium*, brine), but is now generally known as "hydrochloric acid." The acid is less corrosive than sulphuric acid or nitric acid. It acts on the alkalies and dissolves chalk; it dissolves iron and tin, and attacks lead and copper to some extent, but it has no marked action on mercury, silver,

or gold. Glauber (1603–1668), who discovered the method of condensing spirit of salt with the help of water, also examined the residue that was left behind in the retort when oil of vitriol and salt were heated together; it was a salt-like substance, which he called "sal mirabile," but it is now known as GLAUBER'S SALT.

Properties of Mineral Acids.

It will be seen that the properties of mineral acids resemble those of vinegar, but are more strongly developed. The action on the alkalies and on chalk is much more vigorous; and instead of merely corroding a few of the metals, the mineral acids can be used, either alone or in combination, to dissolve all the metals; this important result had already been accomplished in the early alchemistic period.

C.—The Preparation of New Salts.

Artificial Salts.

When acids act on the alkalies, on chalk, or on metals, the effervescence caused by the liberation of gas at once attracts attention; but the watery liquid which remains behind is found to contain equally important products, which may be crystallised out by evaporating the solution. These are all salt-like substances, in the sense of Boyle's definition. Many of them were already familiar; thus it was found that

Muriatic acid and soda	gave	common salt
Muriatic acid and sal volatile	,,	sal ammoniac
Nitric acid and potash	,,	saltpetre or nitre
Nitric acid and soda	,,	Chile saltpetre
Oil of vitriol and soda	,,	Glauber's salt
Oil of vitriol and chalk	,,	gypsum
Oil of vitriol and iron	,,	green vitriol
Oil of vitriol and copper	,,	blue vitriol.

In other cases new products were obtained, for instance,

Lunar caustic * from nitric acid and silver.
Vitriolated tartar from oil of vitriol and potash (or tartar †).

Nomenclature of Salts.

When it was discovered that salts could be prepared artificially, the custom arose of giving to each salt a systematic name describing the acid and the BASE (alkali, earth, or metal) from which it was prepared. This system of nomenclature, which was completed by a group of French chemists (de Morveau, Lavoisier, Berthollet, and Fourcroy) in the year 1787, has survived to the present day in commerce

* Described by Geber, *circ.* 800 A.D. or later.

† "Calcined tartar," or the "burnt lees of wine," was one of the purest forms of potash.

and in pharmacy; in scientific work, however, it has been modified (as described below) as a result of the discovery that the alkalies and earths also contain metals. It had long been known that many of the metals dissolved more easily in acids if they were first burnt or calcined. Thus blue vitriol was prepared by Glauber by the action of *dilute* oil of vitriol on burnt plates of copper; and in the same way the sweet but poisonous salt known as SUGAR OF LEAD was prepared by the action of distilled vinegar on burnt lead or litharge. These metallic calces were very similar to the earths, and, like them, dissolved in acids to form salts; Lavoisier therefore suggested, in 1789, that the earths might be regarded as calces of unknown metals. This suggestion was verified nearly twenty years later by Davy, who isolated from the earths MAGNESIA, LIME, STRONTIA, and BARYTA the four metals MAGNESIUM, CALCIUM, STRONTIUM, and BARIUM. A few months earlier in the same year (1807) Davy had effected the decomposition of the alkalies, potash and soda, and had separated from them the metals POTASSIUM and SODIUM. It was then no longer possible to maintain a distinction between the salts of the alkalies, earths, and metals, since all were alike metallic compounds. The custom therefore arose of describing all salts as derived from a metal and an acid. The three types of nomenclature are shown for six typical "sulphates" in the following table:—

	Early name.	*Lavoisier's name.*	*Modern name.*
Derived from alkalies	Glauber's salt	Sulphate of soda	Sodium sulphate
	Vitriolated tartar	Sulphate of potash	Potassium sulphate
Derived from earths	Epsom salts	Sulphate of magnesia	Magnesium sulphate
	Gypsum	Sulphate of lime	Calcium sulphate
Derived from metals	Green vitriol	Sulphate of iron	Ferrous sulphate
	Blue vitriol	Sulphate of copper	Copper sulphate

In just the same way for other acids we may write:

Saltpetre = nitrate of potash or potassium nitrate
Lunar caustic = nitrate of silver or silver nitrate
Common salt = muriate of soda or sodium chloride *
Sugar of lead = acetate of lead or lead acetate.

Insoluble Salts.

It has already been stated that Boyle used the general term "salt" to describe other soluble substances possessing a saline taste. When the dual character of these salts was realised, a further extension of the definition became necessary. Thus, it was impossible to regard Epsom salts (sulphate of magnesia) as a salt, and to exclude gypsum (sulphate of lime), merely because it was only slightly soluble in water. In the same way, it was necessary to include amongst the salts of the metals not only the freely soluble muriates, or chlorides, of gold, copper, and iron, but also the sparingly soluble chloride of lead, and the almost insoluble chloride of silver. These sparingly

* The term chloride as a substitute for muriate was introduced by Davy in 1816.

soluble salts are often almost tasteless and resemble the earths rather than substances such as common salt. Their classification with the soluble salts is justified, not merely by their similar methods of preparation, but also by their similar chemical properties ; thus, the insoluble muriates or chlorides can be decomposed by heating them with strong sulphuric acid, in just the same way as common salt and the soluble muriates ; in each case, muriatic acid is set free and the muriate is converted into the corresponding sulphate.

The Strength of Acids and Bases. Chemical Affinity.

It has been shown in the preceding paragraphs that oil of vitriol is able to displace both nitric and muriatic acids from their salts. John Mayow (1645–1697), who made a special study of the action of oil of vitriol on nitre, stated that in this process the fixed base of the nitre will "leave its own acid and will enter into union with the acid of the vitriol, which is more concordant with it." The same idea was expressed at a later date by saying that oil of vitriol had a greater CHEMICAL AFFINITY for potash than had nitric acid, or simply that oil of vitriol was the stronger acid ; modern measurements have shown, however, that hydrochloric and nitric acids are stronger than sulphuric acid, which displaces the two preceding acids from their salts on account of its higher boiling-point and not because it is the stronger acid.

Mayow also studied the action whereby sal volatile was prepared by heating sal-ammoniac with one of the fixed alkalies. Under these conditions, the volatile alkali was displaced from its combination with muriatic acid by the fixed alkali, which thus proved itself to be the stronger base. As Mayow put it, the acid "is capable of entering into closer union," (*i.e.*, forming a more stable compound) with any fixed alkali than with a volatile alkali.

Mayow's views as to the strength of acids and bases found expression during the following century in the compilation of TABLES OF AFFINITY. In these tables one base, *e.g.*, potash, was selected, and the different acids were arranged in the order of their affinity for this particular base : similar tables were drawn up for other bases, the order of the acids being changed to correspond with variations of their relative affinities for different bases. In the same way, lists of bases were drawn up in the order of their relative affinities for particular acids.

This attempt to classify chemical affinities was rendered difficult by the fact that the relative affinities were found to depend not only on the nature of the acid and base, but also on the conditions under which they acted upon one another. Thus Mayow showed in 1674 that, when heated together,

nitre and *oil of vitriol* gave *nitric acid* and *vitriolated tartar.**

But Baumé in 1760 showed that by mixing them together in the cold

*vitriolated tartar** and *nitric acid* gave *nitre* and *oil of vitriol.*

When, therefore, in 1775, Bergman attempted to classify all the acids and bases according to their affinity for one another, he was obliged to draw up two series of tables, one showing the order of affinity when the substances were merely mixed together in solution "in the wet way," and another showing their behaviour when heated together "in the dry way." Thus, when tested "in the wet way," phosphoric acid was found to be a very weak acid, since insoluble phosphates were dissolved by sulphuric,

* Sulphate of potash or potassium sulphate.

nitric, and muriatic acids, and even by weak vegetable acids such as acetic acid; but when tested "in the dry way" it behaved as a very strong acid, displacing even oil of vitriol from its compounds. The fact is that the behaviour of acids when heated "in the dry way" depends more on their fixedness or volatility than on inherent strength or weakness; when tested "in the wet way" the solubility or insolubility of the acids becomes an equally important factor. At the present time the strength of acids is usually compared by allowing them to compete together *in solution* for the possession of a base which is not sufficient in quantity to neutralise both. Similar methods are used to compare the relative strengths of bases.

The strength of acids may also be compared by their action on indicators. Thus, indigo retains its blue colour even under the action of the strongest mineral acids, if these are diluted with water. The blue paper in which loaf-sugar was formerly wrapped is reddened by mineral acids, but not by acetic acid. Syrup of violets becomes green on the addition of acetic acid but is not affected by carbonic acid (p. 79). This acid is, however, still strong enough to redden blue litmus, or the extract of blue cornflowers.

Chemical Composition.

The two preceding paragraphs have shown how the study of salt-formation led to the first clear ideas on the subject of chemical affinity. This study played an almost equal part in developing the idea of chemical composition. It was probably the study of metals which first suggested that an element might survive a series of chemical changes and pass undestroyed from one compound to another. Thus it was generally believed that the metals were already present in the ores from which they were "extracted," and equally in the calces and salts derived from them. Similar notions in reference to salts were put forward by Mayow. The recovery of nitric acid from nitre by the action of oil of vitriol, and the recovery of sal volatile from sal-ammoniac by the action of potash, seemed to him to prove that although acids and alkalies "pass into a neutral substance when they meet, yet they do not, as is generally supposed, entirely destroy each other." This idea of the survival of the acid and alkali in a salt from which all their peculiar properties had disappeared marks a very important advance in the conception of chemical composition; it was in complete contrast with the alchemistic idea that the proportions of mercury, sulphur, and salt in a substance could be judged from the predominance of metallic, combustible, or saline qualities, or generally that the properties of a substance were a direct indication of its composition.

SUMMARY AND SUPPLEMENT.

1. **Soluble Salts.**—Amongst the raw materials studied from very early times were a number of SOLUBLE SALTS, characterised by (*a*) solubility in water, (*b*) pungent taste, (*c*) crystalline character. Some of the principal salts known from very early times were as follows:

Common salt	Sodium chloride	$NaCl$
Saltpetre	Potassium nitrate	KNO_3
Sal-ammoniac	Ammonium chloride	NH_4Cl
Alum	Potassium aluminium sulphate	$KAl(SO_4)_2,12H_2O$

Green vitriol	Ferrous sulphate	$FeSO_4,7H_2O$
Blue vitriol	Copper sulphate	$CuSO_4,5H_2O$
Washing soda	Sodium carbonate	$Na_2CO_3,10H_2O$
Potash	Potassium carbonate	K_2CO_3

2. **Mineral Acids.**—From these salts a series of MINERAL ACIDS was prepared as follows :—

(*a*) **Oil of vitriol** or **sulphuric acid,** H_2SO_4, was prepared by distilling alum or partially dried green vitriol :

$2KAl(SO_4)_2$	+	$3H_2O$	=	K_2SO_4	+	Al_2O_3	+	$3H_2SO_4$
Potassium aluminium sulphate		Water		Potassium sulphate		Aluminium oxide		Sulphuric acid
$2FeSO_4$	+	H_2O	=	Fe_2O_3	+	SO_2	+	H_2SO_4
Ferrous sulphate		Water		Ferric oxide		Sulphur dioxide		Sulphuric acid

(*b*) **Aqua fortis** or **nitric acid,** HNO_3, was prepared by distilling saltpetre with oil of vitriol :

KNO_3	+	H_2SO_4	=	$KHSO_4$	+	HNO_3
Potassium nitrate		Sulphuric acid		Potassium hydrogen sulphate		Nitric acid

(*c*) **Spirit of salt,** or **hydrogen chloride,** HCl, was set free as a fuming gas by the action of oil of vitriol on salt. When this gas was dissolved in water, **muriatic acid** or **hydrochloric acid,** HClaq., was produced. The residue from the preparation of spirit of salt consisted of **Glauber's salt,** or **sodium sulphate,** $Na_2SO_4,10H_2O$:

$2NaCl$	+	H_2SO_4	=	Na_2SO_4	+	$2HCl$
Sodium chloride		Sulphuric acid		Sodium sulphate		Hydrogen chloride

3. **Properties of Acids.**—These mineral acids resemble the vegetable acids, such as acetic acid, $C_2H_4O_2$, the acid of vinegar :

(*a*) In their sour taste.
(*b*) In changing the colour of certain INDICATORS.
(*c*) In their power of causing soda to effervesce :

Na_2CO_3	+	H_2SO_4	=	Na_2SO_4	+	H_2O	+	CO_2
Soda		Sulphuric acid		Sodium sulphate		Water		Carbon dioxide
Na_2CO_3	+	$2HNO_3$	=	$2NaNO_3$	+	H_2O	+	CO_2
Soda		Nitric acid		Sodium nitrate				
Na_2CO_3	+	$2HCl$	=	$2NaCl$	+	H_2O	+	CO_2
Soda		Muriatic acid		Salt				

(*d*) In dissolving chalk with effervescence (but sulphuric acid gives an insoluble product) :

$CaCO_3$	+	H_2SO_4	=	$CaSO_4$	+	H_2O	+	CO_2
Chalk		Sulphuric acid		Calcium sulphate				
$CaCO_3$	+	$2HNO_3$	=	$Ca(NO_3)_2$	+	H_2O	+	CO_2
Chalk		Nitric acid		Calcium nitrate				
$CaCO_3$	+	$2HCl$	=	$CaCl_2$	+	H_2O	+	CO_2
Chalk		Muriatic acid		Calcium chloride				

(*e*) In dissolving metals :

Sn	+	2HCl	=	$SnCl_2$	+	H_2		
Tin		Muriatic acid		Stannous chloride		Hydrogen		
Fe	+	H_2SO_4	=	$FeSO_4$	+	H_2		
Iron		Sulphuric acid		Ferrous sulphate				
Zn	+	H_2SO_4	=	$ZnSO_4$	+	H_2		
Zinc		Sulphuric acid		Zinc sulphate				
Cu	+	$2H_2SO_4$	=	$CuSO_4$	+	SO_2	+	$2H_2O$
Copper		Sulphuric acid		Copper sulphate		Sulphur dioxide		
6Ag	+	$8HNO_3$	=	$6AgNO_3$	+	2NO	+	$4H_2O$
Silver		Nitric acid		Silver nitrate		Nitric oxide		
Au	+	$HNO_3 + 4HCl$	=	$HAuCl_4$	+	NO	+	$2H_2O$
Gold		Aqua regia		Aurichloric acid.		Nitric oxide		

The mineral acids differ from the vegetable acids in that all these actions are much more energetic. Thus, aqua fortis and concentrated oil of vitriol are capable of dissolving copper, mercury, and silver, which are but little acted on by vegetable acids, and a mixture of aqua fortis and spirit of salt known as AQUA REGIA was found to dissolve gold.

4. **Preparation of Salts.**—In addition to liberating gas, these actions left behind in solution a series of salts, some of which, when crystallised out from the solution, were found to be identical with salts that were already known. When thus prepared by the action of acids, these salts were described by the name of the acid and of the alkali, earth or metal on which the acid acted. The different methods of naming these salts are set out in the following table.

TABLE 5.—NOMENCLATURE OF SALTS.

	Common name.	*Modern name.*	*Chemical formula.*
(*a*) SULPHATES :			
Sulphate of soda	Glauber's salt	Sodium sulphate	$Na_2SO_4,10H_2O$
Sulphate of potash	Vitriolated tartar	Potassium sulphate	K_2SO_4
Sulphate of magnesia	Epsom salts	Magnesium sulphate	$MgSO_4,7H_2O$
Sulphate of lime	Gypsum	Calcium sulphate	$CaSO_4,2H_2O$
Sulphate of potash and alumina	Alum	Potassium aluminium sulphate	$KAl(SO_4)_2,12H_2O$
Sulphate of iron	Green vitriol	Ferrous sulphate	$FeSO_4,7H_2O$
Sulphate of copper	Blue vitriol	Copper sulphate	$CuSO_4,5H_2O$
(*b*) NITRATES :			
Nitrate of soda	Chile saltpetre	Sodium nitrate	$NaNO_3$
Nitrate of potash	Saltpetre	Potassium nitrate	KNO_3
Nitrate of silver	Lunar caustic	Silver nitrate	$AgNO_3$

TABLE 5.—NOMENCLATURE OF SALTS.—*Continued.*

	Common name.	*Modern name.*	*Chemical formula.*
(c) MURIATES OR CHLORIDES :			
Muriate of soda	Common salt	Sodium chloride	$NaCl$
Muriate of potash	Sylvine	Potassium ,,	KCl
Muriate of magnesia	—	Magnesium ,,	$MgCl_2,6H_2O$
Muriate of lime	—	Calcium ,,	$CaCl_2,6H_2O$
Muriate of silver	Horn silver	Silver ,,	$AgCl$
Muriate of zinc	"Killed spirits"	Zinc ,,	$ZnCl_2,H_2O$
(d) ACETATES :			
Acetate of soda	—	Sodium acetate	$NaC_2H_3O_2,3H_2O$
Acetate of lime	—	Calcium acetate	$Ca(C_2H_3O_2)_2$
Acetate of lead	Sugar of lead	Lead acetate	$Pb(C_2H_3O_2)_2$
Basic acetate of copper	Verdigris	Basic copper acetate	$Cu(C_2H_3O_2)_2 + Cu(OH)_2$.

In the modern names, the salts are all described as derivatives of metals, those derived from soda and potash being described as sodium and potassium salts, whilst salts derived from lime and magnesia are described as calcium and magnesium salts.

5. **Strength of Acids.**—Sulphuric acid will displace nitric acid from salt-petre, and muriatic acid (hydrogen chloride) from salt, *e.g.*, by heating very strongly we get :

$$\underset{\text{Potassium nitrate}}{2KNO_3} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Potassium sulphate}}{K_2SO_4} + \underset{\text{Nitric acid}}{2HNO_3^*}$$

$$\underset{\text{Sodium chloride}}{2NaCl} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Sodium sulphate}}{Na_2SO_4} + \underset{\text{Hydrogen chloride}}{2HCl}$$

Sulphuric acid therefore behaves as if it were a stronger acid than nitric acid or muriatic acid. In the cold, however, these actions may be reversed, *e.g.* :

$$\underset{\text{Potassium sulphate}}{K_2SO_4} + \underset{\text{Nitric acid}}{2HNO_3} = \underset{\text{Potassium nitrate}}{2KNO_3} + \underset{\text{Sulphuric acid}}{H_2SO_4}$$

When mixtures such as these are heated together the "strength" of the acid depends mainly on its fixedness ; thus, even sand or **silica**, SiO_2, which possesses no obvious acid properties, but which can be regarded as the "anhydride" of **silicic acid**, H_2SiO_3 (*i.e.*, as silicic acid minus water), will displace sulphuric acid from its salts, since it boils at a much higher temperature than sulphuric acid.

$$\underset{\text{Potassium sulphate}}{K_2SO_4} + \underset{\text{Silica (sand)}}{SiO_2} = \underset{\text{Potassium silicate}}{K_2SiO_3} + \underset{\text{Sulphuric anhydride}}{SO_3^*}$$

When tested in the cold, however, the insolubility of the acids (or of their salts) is of similar importance ; thus, insoluble silicic acid is precipitated from its salts by sulphuric acid :

$$\underset{\text{Potassium silicate}}{K_2SiO_3} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Potassium sulphate}}{K_2SO_4} + \underset{\text{Silicic acid}}{H_2SiO_3}$$

and even by weak acids such as acetic acid.

* Partial decomposition of these products takes place.

In order to test the strength of acids correctly, therefore, they should be allowed to compete in solution for possession of a base, without being either distilled out or precipitated.

6. **Strength of Bases.**—Similar conditions apply to bases. Thus, the fixed base magnesia will displace the volatile base ammonia from its salts and take possession of the acid :

$2NH_4Cl$	+	MgO	=	$MgCl_2$	+	$2NH_3$	+	H_2O ;
Sal-ammoniac (ammonium chloride)		Magnesia		Magnesium chloride		Ammonia		Water

but in the cold the insoluble base magnesia is partially precipitated from its soluble salts by the soluble base ammonia :

$MgCl_2$	+	$2NH_3$	+	$2H_2O$	=	$Mg(OH)_2$	+	$2NH_4Cl$
Magnesium chloride		Ammonia		Water		Hydrated magnesia		Sal-ammoniac (ammonium chloride)

CHAPTER V

THE CALCINATION OF METALS

The Utility of Metals.

Amongst the substances known from ancient times several METALS were included. These possess a bright METALLIC LUSTRE, that is to say, they are opaque but give polished surfaces which reflect light brilliantly. They also possess valuable mechanical qualities which are almost unknown amongst other types of substances, *e.g.*, TOUGHNESS, MALLEABILITY, DUCTILITY, and in many cases very great STRENGTH (compare Chapter XXX). Metals which possess these properties can be twisted, hammered, or rolled into sheet, drawn into wire, and submitted to great stresses without being fractured. On account of these properties the metals occupy an unique position in industry and manufacture, and every advance in civilisation is marked by new uses to which the metals are put. Until the metals were discovered the only tools were those made from wood, chipped flints, jade or similar materials; and even to-day modern machinery is entirely dependent on metals for all its important structural elements.

The Discovery of the Metals.

Seven metals were known in classical times, namely, **gold, silver, mercury, copper, tin, lead, iron.** These seven metals were known in the alchemistic period as *Sol, Luna, Mercury, Venus, Jupiter, Saturn,* and *Mars.* Some of them were found ready to hand in the form of NATIVE METALS, whilst others were prepared by SMELTING from their ORES, *i.e.*, by heating suitable minerals with charcoal and melting out the metals which they contain.

(*a*) **Gold** (Fig. 39) was probably the first of these seven metals to be discovered and collected. The metal occurs in the free state in minute particles embedded in the rocks; but these particles possess the property of welding together in the cold, so that when the rocks disintegrate and are washed away, the gold becomes clotted together and is found in the form of bright yellow nuggets in the gravel beds of rivers almost all over the globe. On account of its toughness, and the ease with which it can be worked, as well as by reason of its brilliant and permanent lustre, metallic gold has been valued very highly from the earliest times.

(*b*) **Silver** (Fig. 40) is also found in the native state; but it tarnishes more readily than gold and has always been valued at a lower rate.

(*c*) **Mercury,** occurring as minute drops of liquid metal in certain rocks, has always been regarded with peculiar interest; the alchemists, in particular, considered it to be the type or "principle" from which all other metals were derived; it has, however, fewer uses than the solid metals.

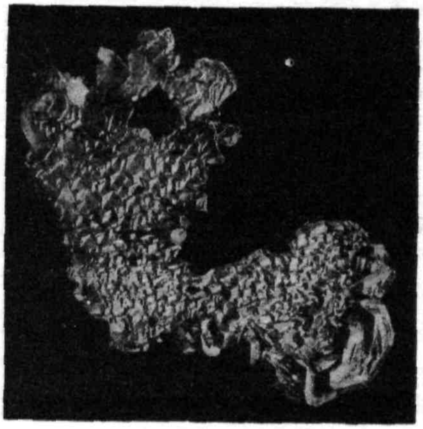


FIG. 39.—NATIVE GOLD.

(*d*) **Copper** is a soft, tough metal, found in the native state or smelted very easily from certain ores. Its value was very greatly enhanced by the discovery that it can be hardened, and thus made fit for the manufacture of tools and weapons, by the addition of metallic tin.

(*e*) **Tin** is obtained by smelting TIN-STONE, a mineral which was discovered and "worked" from very early times in the streams of Cornwall. The ALLOY of copper and tin is known as BRONZE and was the first metal to supersede the flint implements of the Stone Age.

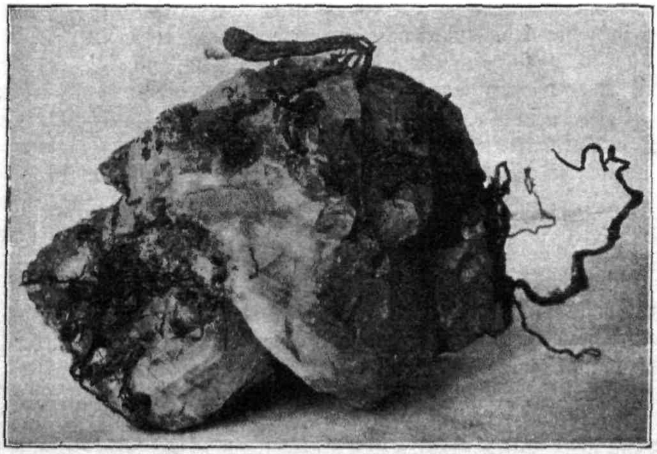


FIG. 40.—NATIVE SILVER.

(*f*) **Lead** was derived in much the same way as tin from the lead ores which are still mined in Derbyshire.

(*g*) **Iron** is much more difficult to smelt than tin, lead, or copper, since it requires a much higher temperature to melt it; the discovery and use of iron appear, therefore, in almost every country, to have followed that of bronze. It is the commonest and by far the cheapest of the metals, and is capable of a larger range of uses than any other metal; the alloys of iron, most of which are described under the general name of STEEL, are unsurpassed in the valuable mechanical properties which they possess.

It may be of interest to note that the prices of the seven metals in 1914 and 1921 were approximately as follows :—

Gold, 85s. (1914) to 108s. (1921) per oz.
Silver, 2s. to 3s. per oz.
Mercury, £11 per 77 lb., or £320 per ton.
Tin, £140 to £170 per ton.
Copper, £60 to £70 per ton.
Lead, £18 to £22 per ton.
Iron, 50s. to £6 per ton.

Noble Metals and Base Metals.

Metals are commonly divided into two groups, the NOBLE METALS, gold and silver, which may be melted in the fire but are not consumed or corroded thereby, and the BASE METALS, which become tarnished, and finally burn away to an earthy product or DROSS.

Noble metals may therefore be purified from base metals by refining in a furnace. Thus copper can be burnt out from gold in the form of a black ash, which can be removed easily from the pure metal. So, also, silver contaminated with lead may be purified by burning away the lead in the form of a hard stony dross to which the name of LITHARGE is given. The name litharge (Greek λίθος, stone, ἄργυρος, silver) suggests the way in which this substance was usually prepared, rather than its composition, since it does not contain any silver. When the litharge is ground to powder and gently roasted, its colour changes from yellowish-brown to scarlet, and a substance is obtained which was used as a pigment in classical times under the name of MINIUM, and is now generally called RED LEAD. When tin is burnt in the same way as lead it becomes covered with a dark powder, but finally yields a pure white product somewhat resembling chalk.

Iron, when burnt, yields a blue-black scale which may be seen round the anvil of a blacksmith's shop and is known as SMITHY SCALE. As the impurities of iron burn more readily than the iron itself, iron is often purified by working the hot metal until the impurities are burnt out of it. This process is known as PUDDLING, and the purified metal is described appropriately as WROUGHT IRON. The blue-black scale from the refinery was used by Priestley under the name of FINERY CINDER.

The white product obtained by burning tin resembles chalk or lime in appearance. Such products were therefore described as CALCES (Latin *calx*, chalk, or lime).* This name was also used in the case of metals which gave rise to coloured products. The burning of the metals was described as CALCINATION.

Metals Increase in Weight on Calcination.

The fact that metals gain in weight when burnt was described and discussed in 1630 by a French doctor named Jean Rey, in an "Enquiry into the Cause wherefore Tin and Lead increase in Weight on Calcination." He records the astonishment of a neighbouring apothecary when from 2 lb. 6 oz. of fine English tin he obtained not less than 2 lb. 13 oz. of white calx. Evidence was also quoted to show that "lead on calcination increases in weight by eight or ten pounds per cent." After examining various alternative hypotheses, Rey suggested that the gain in weight must be due to the condensation of air upon the metal.

Robert Boyle, in 1673, showed that a gain in weight occurs not only in the burning of tin and lead but also of copper and iron, but he attributed it to the absorption of heat from the fire in the form of "igneous particles." This view was disproved a century later by Lavoisier (1774), who calcined tin in sealed glass vessels, and showed that no marked change in weight took place until the vessel was broken open. Lavoisier therefore concluded that the gain in weight of the calcined metal did not come from the fire nor from anything outside the flask, but was due to the absorption of a part of the air which the flask contained. When the flask was opened air rushed in and the flask became heavier by an amount which was almost exactly equal to the gain in weight of the tin.†

Law of Conservation of Weight or Mass. The Indestructibility of Matter.

Lavoisier's experiment was of great importance as showing that heat is not a material substance, *i.e.*, it has no mass or weight and cannot be detected by means of the balance. It also showed that there is no alteration in the total mass or weight of the substances concerned in the chemical change. This statement is commonly known as the LAW OF CONSERVATION OF MASS or of the INDESTRUCTIBILITY OF MATTER. It was on the results of observations such as these that Lavoisier based his idea of a CHEMICAL EQUATION, that is, an equation in which the materials used are set out on one side of the sign of equality

* In their behaviour towards acids the calces resemble lime so closely that Lavoisier in 1789 urged that lime and the earths must be regarded as calces of unknown metals.

† From the fact that these weights were so nearly equal, Lavoisier concluded that the part of the air which combines with the metal during calcination has almost the same density as atmospheric air.

and the products on the other. If all these materials are weighed the total weight must be the same on each side of the equation.

The Law of Constant Composition verified by Experiments on Calcination.

In Lavoisier's experiments, calcination was incomplete because only a limited quantity of air was provided. When, however, the calcination is continued until the whole of the metal has been burnt, there is found to be a definite ratio between the weight of the metal and that of the calx produced from it. Thus, Proust, in 1799 directed attention to the fact that the black calx of copper was always 25 per cent. heavier than the metal, whether it was prepared from it by direct calcination or indirectly by dissolving in nitric acid, precipitating with alkali, and igniting the residue. It was by observations of this kind that he established the LAW OF CONSTANT COMPOSITION.

Air a Mixture.

Lavoisier's experiments on the calcination of tin showed also that only a limited quantity of metal could be calcined in a given quantity of air, and that a greater quantity was calcined in a large than in a small retort. Even in the small retort only about one-fifth of the air was absorbed, the remaining four-fifths being composed of a gas which could not be used to bring about calcination. In the same way, he showed that the vigorous burning of phosphorus only diminished the volume of air by about one-fifth; the remaining four-fifths, which was slightly less dense than atmospheric air, was no longer fit for the respiration of animals or for the combustion or calcination of substances. This inactive residue, which Lavoisier called AZOTE (Greek *ἀ* not, *ζωή* life) because it does not support life, is composed chiefly of a gas which is now known as NITROGEN, because it is one of the chief constituents of nitre.

The diminution of air by breathing and burning had been discovered a hundred years earlier (in 1674) by John Mayow. It was studied very fully by the Swedish chemist Scheele, who showed that the active part of the air could be removed by many different methods, *e.g.*, by rusting iron, and by burning or smouldering phosphorus. The residue of "foul air" was useless for breathing and burning; but in no case was the volume of the air diminished beyond about one-fifth.

Discovery of Oxygen, the Active Constituent of Air.

Whilst the inactive residue could be prepared easily by many different methods, Lavoisier found very great difficulty in recovering the active part of the air which was used up in burning and breathing. The discovery of a convenient method was brought to his notice by Priestley in 1774. It has been shown above that metals may be divided into two classes: noble metals, silver and gold, which do not tarnish

when heated, and base metals, such as copper, lead, tin, or iron, which are converted into calces by heating in the air. Mercury occupies an intermediate position; when heated gently it is converted into a red calx, "mercurius calcinatus per se"; but when this calx is heated, the mercury is "revivified" and recovered in the metallic state. Priestley, whilst searching for new gases, studied the action of heat on many substances, amongst which the calx of mercury was included. He found that a gas was expelled from it, and was much astonished to discover that this was even more active than ordinary air; thus, a candle burnt in the gas with a remarkably vigorous flame, and red-hot wood sparkled in it and burnt away rapidly; a mouse placed in the gas remained at ease twice as long as when enclosed in ordinary air. The same gas was also obtained by heating red lead, the red substance obtained by gently roasting litharge in air (p. 60). Quite independently of Priestley, Scheele prepared the same gas by decomposing the vapour of nitric acid by heat, and subsequently in a more convenient way by the action of heat on saltpetre, and upon the black mineral now known as PYROLUSITE.

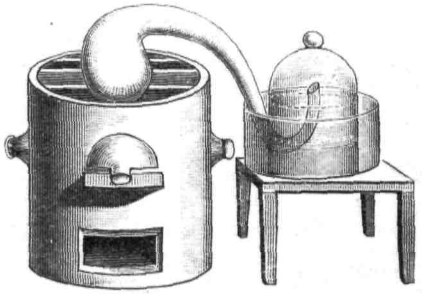


FIG. 41.—LAVOISIER'S APPARATUS FOR CALCINATION OF MERCURY.

Lavoisier's Experiments on the Calcination of Mercury.

Lavoisier had already shown by quantitative experiments that the calx of tin was formed by the combination of the metal with a part of the air and not by the absorption (or loss) of igneous particles from the fire.

In order to complete his theory of combustion, Lavoisier was very anxious to procure in a free state the air which he assumed to be present in the calx. Priestley's observation gave him exactly what he wanted. The calx of mercury could not only be prepared in the same way as the calx of tin, but by further heat could be decomposed, thus:—

(i) *Preparation of calx* Metal + air = calx
(ii) *Decomposition of calx* Calx = metal + active air.

Lavoisier carried out these experiments quantitatively, using the apparatus shown in Fig. 41. Four ounces of mercury were heated in a retort the neck of which was bent so that it passed up into a bell-jar of air inverted over mercury. After heating for twelve days the air in the bell-jar and retort had been diminished from 50 to 42 or 43 cubic inches, and 45 grains of calx had been produced; the air which remained was no longer fit for respiration or combustion. The 45 grains

of calx, when decomposed in a small retort, gave $41\frac{1}{2}$ grains of mercury and 7 or 8 cubic inches of Priestley's gas, weighing from $3\frac{1}{2}$ to 4 grains. The whole of the 7 or 8 cubic inches of air that had been absorbed had thus been recovered in a pure state; and the quantities of mercury and gas were just those that were required to make the equation balance, thus—

Red calx	=	Mercury	+	active air
45	=	$41\frac{1}{2}$	+	$3\frac{1}{2}$ grains.

Lavoisier's "Oxygen" Theory of Combustion and of the Composition of Salts.

Boyle thought that the combustion of a metal was due to the *absorption* of igneous particles from the fire. Becher and Stahl, a few years later, suggested that the burning of a metal to an incombustible calx was due to the *escape* from it of fire or phlogiston. Lavoisier, on the other hand, believed and had now been able to prove that the most important feature of the calcination was not the absorption of fire or the loss of inflammability, but the fixation by the metal of an active constituent of the air. He had no difficulty in showing that this constituent was concerned not only in the burning of metals and in breathing, but also in the combustion of inflammable substances such as sulphur and phosphorus. These substances gave rise, not to earthy calces, but to products which dissolved in water to form acid solutions. Lavoisier regarded this production of acids as the chief property of the active gas and he therefore called it OXYGEN (Greek ὀξύς, acid, γεννάω, I beget; compare German, *Sauerstoff*). This name has been retained to the present day, in spite of the fact that many acids are known which contain no oxygen. Compounds in which oxygen was present were described by Lavoisier as OXIDES. Under this title were included, not only the acid oxides of sulphur and phosphorus, but also the basic oxides derived from the metals.

According to Lavoisier's view, all salts were formed by the union of the basic oxide of a metal with the acid oxide of a non-metal, *e.g.*,

$$\left.\begin{array}{l}\left.\begin{array}{l}\text{Lead}\\ \text{Oxygen}\end{array}\right\} = \text{Litharge}\\ \left.\begin{array}{l}\text{Sulphur}\\ \text{Oxygen}\end{array}\right\} = \begin{array}{l}\text{Sulphuric}\\ \text{anhydride*}\end{array}\end{array}\right\} = \text{Lead sulphate.}$$

A large number of salts are actually of this type, containing a metal, a non-metal, and oxygen; these ternary compounds, containing three elements, of which one is oxygen, are called OXY-SALTS. Common salt, however, does not contain any oxygen, but is a binary compound of the metal SODIUM with a pungent gas, CHLORINE (p. 268), which can be set free by the action of oxygen or of oxidising

* Lavoisier called the oxide of sulphur *sulphuric acid*; but as it becomes acid only when dissolved in water it is now generally called *sulphuric anhydride*.

agents on "spirit of salt." The composition of common salt is therefore analogous to that of the oxides which are formed by direct combination of the metals with oxygen.

These salt-like binary compounds of the metals with chlorine are known as CHLORIDES. They differ from the oxy-salts in that they contain no oxygen, and this is true also of the acid gas, SPIRIT OF SALT, which is set free from them by the action of oil of vitriol. As a general class the binary salts are distinguished as HALOID SALTS, being formed by direct combination of a metal with a HALOGEN or salt-producing element (Greek, ἅλς, salt, γεννάω, I beget) instead of by combination of the basic oxide of a metal with the acid oxide of a non-metal.

The Oxidation of Mercury as a Reversible Action.

It will be noticed that the interaction between mercury and oxygen is reversible. At a low temperature the action may be represented by the equation:

$$\text{mercury} \quad + \quad \text{oxygen} \quad = \quad \text{red calx.}$$

At a higher temperature the equation is:

$$\text{red calx} \quad = \quad \text{mercury} \quad + \quad \text{oxygen.}$$

These two actions can be combined in one equation as follows:

$$\text{red calx} \underset{\text{LOW TEMPERATURE}}{\overset{\text{HIGH TEMPERATURE}}{\rightleftarrows}} \text{mercury} + \text{oxygen.}$$

REVERSIBLE ACTIONS are of great importance in industrial operations; they have the great advantage that the raw materials can be reproduced from the product, and so used over and over again. Thus, oxygen was prepared commercially for many years by making use of the reversible oxidation of BARYTA (p. 645), an earth closely resembling lime. When heated in air the baryta absorbs oxygen and is converted into a substance known as BARIUM PEROXIDE. When the temperature is raised or the pressure reduced, the peroxide decomposes again into baryta and oxygen:

$$\text{baryta} + \text{oxygen} \underset{\substack{\text{LOW PRESSURE OR} \\ \text{HIGH TEMPERATURE}}}{\overset{\substack{\text{HIGH PRESSURE OR} \\ \text{LOW TEMPERATURE}}}{\rightleftarrows}} \text{barium peroxide.}$$

In practice the temperature was kept constant at a bright cherry-red heat. Air was pumped in under an excess pressure of about one atmosphere during a period of ten minutes, when oxygen was absorbed and the inactive residue escaped from a valve. The pumps were then reversed, when oxygen was drawn out and compressed into steel cylinders.

SUMMARY AND SUPPLEMENT.

1. **The Metals.**—Amongst the substances known from very early times were seven metals—

	Latin names.	Chemical symbols.
Gold	Aurum	Au
Silver	Argentum	Ag
Mercury	Hydrargyrum	Hg
Copper	Cuprum	Cu
Tin	Stannum	Sn
Lead	Plumbum	Pb
Iron	Ferrum	Fe

With the exception of tin and lead, these were all found as metals, including meteoric iron, but copper, tin, lead, and iron were usually prepared by smelting ores, *i.e.*, by heating certain minerals in a charcoal-fire until the metal melted out from them.

2. **Burning of Metals.**—The NOBLE METALS, gold and silver, do not tarnish when heated in the air, but the BASE METALS, copper, tin, lead, and iron, burn away to an earthy product or dross. Thus :

(*a*) **Lead** burns to LITHARGE, and on further roasting gives MINIUM or RED LEAD :

$$2Pb + O_2 = \underset{\text{Litharge}}{2PbO}$$

$$6PbO + O_2 = \underset{\text{Red lead}}{2Pb_3O_4}.^*$$

(*b*) **Iron** burns to a blue-black compound known as SMITHY SCALE or FINERY CINDER :

$$3Fe + 2O_2 = \underset{\text{Smithy scale}}{Fe_3O_4}.$$

(*c*) **Tin** burns to a white powder :

$$Sn + O_2 = SnO_2.$$

The chalk-like character of the product led to the general name of CALX for these products, whilst the process of burning was called CALCINATION.

3. **Azote and Oxygen.**—Calcination of metals is accompanied by a gain in weight, *which was attributed by Boyle in 1673 to the absorption of igneous* particles from the fire, and by Becher and Stahl to the escape of fire or phlogiston, which was assumed to have a negative weight. Lavoisier in 1772 showed that there was no change of weight when tin was calcined in a sealed flask until the flask was opened and air rushed in ; the gain in weight was due to the absorption by the metal of an active part of the air, leaving behind a residue, unfit for combustion or respiration, to which Lavoisier gave the name AZOTE. The active part of the air can be recovered by heating the red calx of mercury, an element which behaves as a base metal at low temperatures, but as a noble metal when heated more strongly :

$$2Hg + O_2 \underset{500^\circ}{\overset{300^\circ}{\rightleftarrows}} 2HgO.$$

* Red lead as commonly prepared is not a pure substance and contains less oxygen than is required by this formula.

It was named OXYGEN by Lavoisier because it was active in converting sulphur and phosphorus into acids :

$$S + O_2 = SO_2 \text{ (Sulphur dioxide)} ; \quad 2SO_2 + O_2 + 2H_2O = 2H_2SO_4 \text{ (Sulphuric acid)}$$

$$P_4 + 5O_2 = P_4O_{10} \text{ (Phosphoric oxide)} ; \quad P_4O_{10} + 6H_2O = 4H_3PO_4 \text{ (Phosphoric acid)}$$

4. **Reversible Oxidation.**—The oxidation of mercury is a reversible change, as shown by the arrows in the equation which is set out in the preceding paragraph. Oxygen was prepared commercially for many years by means of a similar reversible action in which baryta was used instead of mercury :

$$\underset{\text{Baryta}}{2BaO} + \underset{\text{Oxygen}}{O_2} \rightleftarrows \underset{\text{Barium peroxide}}{2BaO_2},$$

the action being reversed by changes of pressure instead of by changes of temperature.

5. **Composition of Acids.**—Lavoisier thought that all acids were oxides and that all salts were ternary compounds formed by the union of the basic oxide of a metal with the acid oxide of a non-metal. Common salt, NaCl, however, is a binary compound of sodium with chlorine and does not contain any oxygen ; and the acid set free from it by the action of sulphuric acid is not an oxide but a hydride :

$$\underset{\text{Salt}}{2NaCl} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Sodium sulphate}}{Na_2SO_4} + \underset{\text{Hydrogen chloride}}{2HCl}.$$

Acids are therefore now regarded as *compounds of hydrogen* (usually with a sour taste and possessing the power of changing the colour of indicators) *which contain hydrogen that can be displaced by metals, e.g.* :

$$\underset{\text{Sulphuric acid}}{H_2SO_4} + \underset{\text{Zinc}}{Zn} = \underset{\text{Zinc sulphate}}{ZnSO_4} + \underset{\text{Hydrogen}}{H_2}$$

$$\underset{\text{Hydrogen chloride}}{2HCl} + \underset{\text{Zinc}}{Zn} = \underset{\text{Zinc chloride}}{ZnCl_2} + \underset{\text{Hydrogen}}{H_2}.$$

Sulphuric acid, H_2SO_4, is included in this category as a hydrogen compound ; and the oxide, SO_3, which Lavoisier called sulphuric acid, is now known as **sulphuric anhydride,** *i.e.*, sulphuric acid minus water.

$$\underset{\text{Sulphuric anhydride}}{SO_3} + \underset{\text{Water}}{H_2O} = \underset{\text{Sulphuric acid}}{H_2SO_4}.$$

6. **Composition of Salts.**—Salts are of four principal types.

(i) *Halogen-salts, i.e.*, binary compounds formed by direct combination of a metal with a non-metal, *e.g.* :

$$\underset{\text{Zinc}}{Zn} + \underset{\text{Chlorine}}{Cl_2} = \underset{\text{Zinc chloride}}{ZnCl_2}$$

$$\underset{\text{Tin}}{Sn} + \underset{\text{Chlorine}}{2Cl_2} = \underset{\text{Stannic chloride}}{SnCl_4}.$$

(ii) *Double oxides* or oxy-salts (Lavoisier) :

$$\underset{\text{Lead oxide}}{PbO} + \underset{\text{Sulphur trioxide}}{SO_3} = \underset{\text{Lead sulphate}}{PbSO_4}.$$

(iii) *Double hydrides, e.g.*, sal-ammoniac:

$$\underset{\text{Ammonia}}{NH_3} + \underset{\text{Hydrogen chloride}}{HCl} = \underset{\text{Sal-ammoniac (ammonium chloride)}}{NH_4Cl}.$$

(ii) and (iii) are ternary compounds.

(iv) *Quaternary salts* formed by the union of a basic hydride with an acid oxide and with water, *e.g.*:

$$\underset{\text{Ammonia}}{2NH_3} + \underset{\text{Water}}{H_2O} + \underset{\text{Sulphur trioxide}}{SO_3} = \underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4}.$$

CHAPTER VI

CHALK, LIME, AND THE ALKALIES

The Burning of Chalk to Lime.

From very early times chalk has been "burnt" in order to convert it into lime. This process is carried out in a LIME-KILN (Fig. 42) in which coal and chalk or limestone are burnt in a current of air. The QUICKLIME, which is drawn out from the bottom of the kiln, is acted on very energetically by water. So much heat is generated that clouds of steam are formed, which cause the hard quicklime to swell up and crumble to a fine powder known as SLAKED LIME. Freshly-prepared lime is often described as CAUSTIC LIME from its corrosive action on the skin: it retains its corrosive properties even after slaking and is used in this form for removing the hair from hides. A lime-kiln arranged so as to make use of the gaseous products of combustion is shown in Fig. 177, p. 456.

Lime can also be produced by "burning" a large number of other materials which are described under the general name of LIMESTONE. Thus, lime is made from chalk in the South and East of England, from hard limestone in the North and West; it can also be made by burning marble, coral, and oyster shells with the help of a fire. The burning of chalk and the slaking of lime are very generally carried out with a view to preparing MORTAR for building. The mortar is a mixture of slaked lime and sand, which gradually sets, and cements the bricks or stones of the building firmly together: the minute subdivision of the lime during slaking is an important factor in making the mortar set both quickly and firmly.

At one time it was thought that the conversion of chalk to lime (like the smelting of a metal from its ore or calx) was due to the absorption of phlogiston from the fire, thus:

calx + phlogiston = metal
chalk + phlogiston = lime.

On this hypothesis lime was more complex than chalk, just as a metal was a more complex substance than its calx; but both theories were proved to be wrong as soon as attention was paid to the relative weights of these substances.

Change of Weight in Burning Chalk to Lime.

Joseph Black in 1755 showed that chalk lost in weight to the extent of 44 per cent. when it was burnt to lime. It is not easy to burn the chalk effectively in a closed vessel in such a way as to collect the volatile products; but Black was able to quote an experiment in which chalk had been heated very strongly in an earthenware retort in order to find out whether the loss in weight was due to the escape of a vapour. Although the chalk lost very considerably in weight, only a few drops of water could be condensed. Black therefore concluded that the loss in weight was due to the escape of a gas to which he gave the name of FIXED AIR, thus:

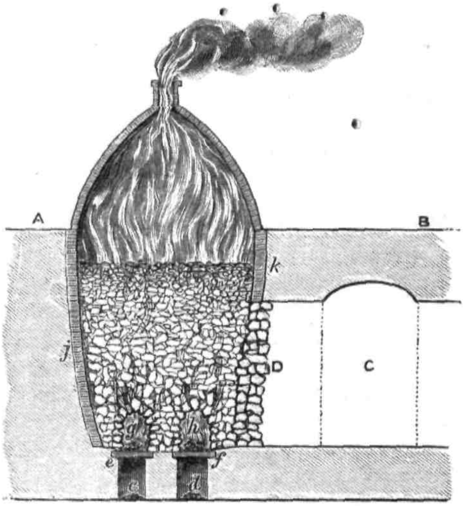


FIG. 42.—SECTION AND

AB. Roof. *C*. Side-arch or "hatch," through which lime is drawn out when burnt. *D*. Side-opening of kiln, built up with lumps of chalk and closed with lime-dust.

chalk	=	lime	+	fixed air
100 parts		56 parts		44 parts.

In the process of slaking, the place of the fixed air is taken by a smaller weight of water, so that

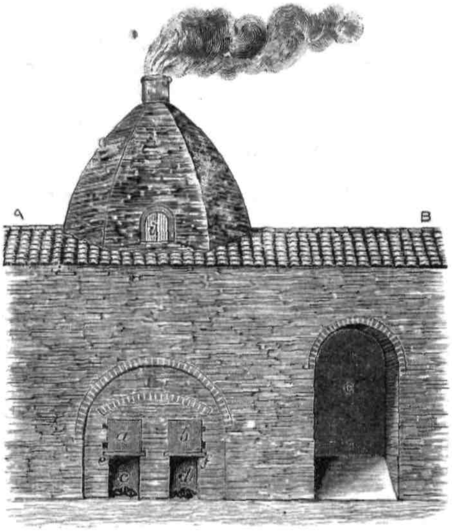
slaked lime	=	lime	+	water
74 parts		56 parts		18 parts.

The Properties of "Fixed Air."

The gas which Black called "fixed air" is now generally known as CARBONIC ANHYDRIDE or CARBON DIOXIDE. At the time when he discovered it, Black did not make any detailed study of its properties; he did not even collect a specimen of the gas over water or over mercury. Its physical properties were, however, examined in 1766 by Cavendish, who found that it was 1·57 times heavier than air and 511 times lighter than water. He showed that the gas dissolved in its own volume of water, but that it could be stored permanently in a bottle inverted in a basin of mercury.

Fixed Air is present in Common Air and in Air dissolved in Water.

Black found that a solution of lime, in the form of LIME-WATER, was reconverted into chalk when exposed to the air. He therefore concluded that fixed air was present in common air; but as lime-water could be preserved for a long time in loosely stoppered bottles, it was evident that the fixed air formed only a small proportion of common air; the actual proportion in the open air is about 3 parts in 10,000.



ELEVATION OF A LIME-KILN.
ab furnace doors; *cd* ash-pits; *ef* fire-bars; *gh* burning fuel; *jk* firebrick lining; *i* inspection-doors.

Black also found that when lime was dissolved in common water, in order to prepare lime-water, a small amount of chalk was always formed and remained undissolved. The air dissolved in water therefore contained fixed air; but again the proportion was only small, since under an exhausted receiver a similar quantity of air escaped from common water and from water from which the fixed air had been removed by the addition of lime.

The Action of Acids on Chalk.

(*a*) Black showed that exactly the same amount of acid was required to dissolve chalk whether it was used as such or was first burnt to lime. In the former case effervescence took place and fixed air escaped; in the latter case the action was similar, but there was no effervescence and no liberation of fixed air.

(*b*) The loss of weight due to the liberation of fixed air by acids was equal to the loss of weight when the fixed air was driven out by burning chalk to lime.

(*c*) The action of acids on chalk evidently consisted, therefore, in an attack upon the lime, in the course of which it was compelled to relinquish its hold upon the fixed air. Thus,

chalk and *muriatic acid* gave *muriate of lime* and *fixed air*
lime and *muriatic acid* gave *muriate of lime* (but *no fixed air*).

(*d*) The action of acids on lime is very similar to their action on metallic calces. Thus,

zinc white and *muriatic acid* give *muriate of zinc* and *no fixed air*.

(*e*) A still closer similarity between the behaviour of the "earths" and the metallic calces is found in the case of the earth MAGNESIA, which is described in the following paragraph and which resembles zinc white in almost all its important properties. This close analogy led Lavoisier in 1789 to conclude that the earths were calces of unknown metals. This hypothesis was verified when Davy in 1807 isolated the metals from them and reconverted metallic calcium, for instance, into quicklime by burning it in air.

The Burning of Magnesia.

The burning of chalk to lime takes place easily only when the process is carried out in a lime-kiln in which the fixed air is carried away by a draught as fast as it is set free. The earth MAGNESIA, on the other hand, is decomposed so easily that it can be burnt without difficulty even in a glass retort. This earth had been prepared by the action of a mild alkali on nitrate of magnesia contained in the "mother of nitre" which remained behind from the preparation of nitre. Black prepared it by the action of an alkali on "bittern" (p. 26), the bitter mother-liquor from sea-salt, in which it is present mainly as a muriate or chloride. He also prepared it from Epsom salts (pp. 26 and 622), in which it occurs as a sulphate. He found that, when heated in a glass retort, it lost more than half its weight, but only a few drops of water were condensed in the receiver; the loss in weight was therefore due to the escape of a gas. This gas was proved to be identical with the "fixed air" of chalk by digesting the original magnesia with lime-water, which was thereby reconverted into chalk, leaving behind nothing but pure water. The original magnesia, which was thus shown to be a compound of an earth with fixed air, resembled chalk in effervescing with acids, and in giving rise to a characteristic series of salts. After calcination, it dissolved like lime without effervescence, having lost its gas already under the influence of heat; it did not, however, dissolve in water, as in the preparation of lime-water, nor combine with water as in the slaking of lime. The ready decomposition of magnesia provided Black with the clue which enabled him to solve the more difficult problem of the burning of chalk to lime.

Fixed Air is present in the Mild Alkalies, Soda and Potash.

It had been known from early times that the mild alkalies could be converted into CAUSTIC ALKALIES by boiling them with a sludge of slaked lime. These caustic alkalies were used in the manufacture of soap and were often described as "soap-lye." Black showed that the caustic alkalies did not contain any lime, but owed their caustic properties to the removal of fixed air from the mild alkalies. The presence

of this gas in the mild alkalies was proved by burning 120 grains of chalk to 68 grains of lime, and then digesting it with a mild alkali, when 118 grains of chalk were recovered. This process is not a simple transfer of fixed air, but an interchange of fixed air and water, thus:

slaked lime	+	*potash*	=	*chalk*	+	*caustic potash*
(lime + water)		(x + fixed air)		(lime + fixed air)		(x + water)

where x is an anhydrous compound analogous with quicklime. In other words, the caustic alkalies, which are actually prepared in contact with water, must be compared, not with quicklime, but with slaked lime.

The mild alkalies differ from chalk, and the caustic alkalies from slaked lime, mainly in their much greater solubility in water. Thus, whilst the solubility of lime is less than 2 grams per litre, caustic soda will dissolve in its own weight of water, and caustic potash in half its weight of water.

The substances which combine with fixed air to form the mild alkalies, and with water to form the caustic alkalies, cannot be prepared directly by igniting these substances; but Davy prepared them by burning the metals POTASSIUM and SODIUM, which he isolated by the action of an electric current on caustic potash and caustic soda; they are, in fact, simple oxides of these metals, just as lime is an oxide of calcium.

Black found that the caustic alkalies were too corrosive to be separated by concentrating their solutions in an earthenware dish, but he obtained them in a pure state by evaporating in a silver dish. As they are easily melted and intensely soluble in water, they do not crystallise when their solutions are boiled down to dryness, but are obtained in the form of a fused mass which can be cast into sticks, or poured into iron drums when prepared commercially.

Fixed Air is present in Sal Volatile.

Black showed that fixed air was also present in the solid volatile alkali, "sal volatile," prepared by heating sal-ammoniac with mild soda or potash. When the fixed air was removed from it by means of lime or a caustic alkali, a pungent liquid, which had long been familiar as SPIRITS OF HARTSHORN, was produced. This liquid is a solution in water of a gas to which Bergman in 1782 gave the name AMMONIA.

The Estimation of Fixed Air.

The amount of fixed air in different substances was estimated in 1766 by Cavendish, who determined the loss in weight caused by the effervescence and escape of gas under the influence of acids. Cavendish's apparatus is shown in Fig. 43. The acid was contained in a bottle, *A*, provided with a trap, *C*, filled with blotting paper to prevent the escape of spray: after weighing, the substance was dropped in to

the bottle, and the trap was fixed by a lute of almond-powder and glue. The loss of weight was determined directly, but a small correction was needed for the extra density of the fixed air remaining in the bottle at the end of the experiment, as compared with the common air which filled it originally. Cavendish found that:

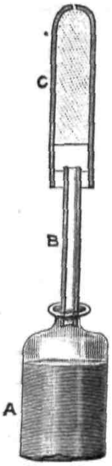


FIG. 43.
CAVENDISH'S APPARATUS FOR FINDING THE WEIGHT AND DENSITY OF GASES.

> 1000 parts of marble lost 407 parts of fixed air
> 1000 parts of sal volatile lost 528 to 538 parts of fixed air
> 1000 parts of pearl-ashes lost 284 to 287 parts of fixed air
> 1000 parts of a crystallised salt obtained by saturating pearl-ashes with fixed air lost 423 parts of fixed air.

SUMMARY AND SUPPLEMENT.

1. **Chalk,** or calcium carbonate, $CaCO_3$, when "burnt" to **quicklime,** or calcium oxide, CaO, loses 44 per cent. by weight of "fixed air" (Black, 1755) or carbon dioxide, CO_2.

$CaCO_3$	=	CaO	+	CO_2
Chalk 100 parts		Quicklime 56 parts		Fixed air 44 parts

On slaking, the 44 parts of "fixed air" are replaced by 18 parts of water, and **slaked lime,** or calcium hydroxide, $Ca(OH)_2$, is produced.

CaO	+	H_2O	=	$Ca(OH)_2$
Quicklime 56 parts		Water 18 parts		Slaked lime 74 parts

The same weight of "fixed air" is set free by the action of acids on chalk, *e.g.*, when muriatic acid is used.

$CaCO_3$	+	2HCl	=	$CaCl_2$	+	H_2O	+	CO_2
Chalk or Calcium carbonate 100 parts		Muriatic acid or Hydrogen chloride 73 parts		Muriate of lime or Calcium chloride 111 parts		Water 18 parts		Fixed air or Carbon dioxide 44 parts

If the chalk is first burnt to lime, no gas is liberated, but the same weight of acid is used and the same weight of calcium chloride is produced.

CaO	+	2HCl	=	$CaCl_2$	+	H_2O
56 parts		73 parts		111 parts		18 parts

This action was used by Berzelius in 1811 to determine the weight of metal in chalk and lime. Ten grams of chalk gave 10·96 grams of calcium chloride. This gave 2·573 times its weight of silver chloride containing 75·3 per cent. of silver and therefore 24·7 per cent. of chlorine. The weight of chlorine in the calcium chloride was therefore $10{\cdot}96 \times 2{\cdot}573 \times 0{\cdot}247 = 6{\cdot}94$ grams and the weight of metallic calcium $10{\cdot}96 - 6{\cdot}94 = 4{\cdot}02$ or about 40 per cent. of the weight of chalk.

Slaked lime can be reconverted quantitatively into chalk by exposure

to common air or to air dissolved in water, both of which contain a small proportion of "fixed air" or carbon dioxide.

$Ca(OH)_2$	+	CO_2	=	$CaCO_3$	+	H_2O
Slaked lime				Chalk		

2. **Magnesia,** or magnesium carbonate, $MgCO_3$, precipitated from its nitrate, $Mg(NO_3)_2$, chloride, $MgCl_2$, or sulphate, $MgSO_4$, by the action of a mild alkali, is an earth resembling chalk very closely.

$Mg(NO_3)_2$	+	Na_2CO_3	=	$MgCO_3$	+	$2NaNO_3$
Magnesium nitrate		Sodium carbonate		Magnesium carbonate		Sodium nitrate
$MgCl_2$	+	Na_2CO_3	=	$MgCO_3$	+	$2NaCl$
Magnesium chloride						
$MgSO_4$	+	Na_2CO_3	=	$MgCO_3$	+	Na_2SO_4
Magnesium sulphate						

It is, however, decomposed by very gentle heating, liberating a large weight of gas.

$$MgCO_3 = MgO + CO_2$$

This gas is "fixed air," since slaked lime in the form of lime-water can be reconverted into chalk by the action of magnesia.

$$MgCO_3 + Ca(OH)_2 = Mg(OH)_2 + CaCO_3.$$

Magnesia dissolves in acids with effervescence, liberating fixed air; when calcined it dissolves in the same way but without liberating gas.

$$MgCO_3 + 2HCl = MgCl_2 + H_2O + CO_2$$
$$MgO + 2HCl = MgCl_2 + H_2O$$

3. **Soda,** or sodium carbonate, Na_2CO_3, and **potash**, or potassium carbonate, K_2CO_3, also contain "fixed air," since they will reconvert slaked lime quantitatively into chalk.

Na_2CO_3	+	$Ca(OH)_2$	=	$2NaOH$	+	$CaCO_3$
Soda or Sodium carbonate		Slaked lime or Calcium hydroxide		Caustic soda or Sodium hydroxide		Chalk or Calcium carbonate
K_2CO_3	+	$Ca(OH)_2$	=	$2KOH$	+	$CaCO_3$
Potash or Potassium carbonate		Slaked lime or Calcium hydroxide		Caustic potash or Potassium hydroxide		Chalk or Calcium carbonate

They are therefore analogous with chalk, from which they differ (i) in being soluble in water, and (ii) in being much more stable towards the action of heat, since the "fixed air" cannot be removed by "burning." The CAUSTIC ALKALIES, sodium hydroxide, NaOH, and potassium hydroxide, KOH, which are produced when fixed air is removed from the MILD ALKALIES, or carbonates, by the action of lime, are analogous to slaked lime, $Ca(OH)_2$, but are very soluble in water and extremely caustic; they can, however, be separated from water by evaporating in a silver (or iron) dish, when a fused product is obtained which solidifies on cooling. The oxides Na_2O and K_2O, analogous to quicklime, CaO, cannot be prepared directly from the alkalies, but are obtained by oxidising the metals sodium and potassium.

The mild alkalies, or carbonates, effervesce with acids, like chalk, liberating fixed air or carbon dioxide.

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$$
$$K_2CO_3 + 2HCl = 2KCl + H_2O + CO_2$$

The caustic alkalies, like lime, do not liberate any gas, but give the same saline product as the corresponding mild alkalies.

$$NaOH + HCl = NaCl + H_2O$$
$$KOH + HCl = KCl + H_2O$$

4. **Sal-ammoniac,** or ammonium chloride, NH_4Cl, gives **sal volatile,** *i.e.*, ammonium carbonate, $(NH_4)_2CO_3$, or ammonium carbamate, $(NH_3)_2CO_2$, when distilled with a mild alkali.

	$2NH_4Cl$	+	Na_2CO_3	=	$2NaCl$	+	$(NH_4)_2CO_3$			
	Sal-ammoniac		Soda		Salt		Ammonium carbonate			
or	$2NH_4Cl$	+	Na_2CO_3	=	$2NaCl$	+	$(NH_3)_2CO_2$	+	H_2O	
	Sal-ammoniac		Soda		Salt		Ammonium carbamate		Water	

These two compounds also effervesce with acids, liberating fixed air, *e.g.*,

$$(NH_4)_2CO_3 + 2HCl = 2NH_4Cl + CO_2 + H_2O$$
$$(NH_3)_2CO_2 + 2HCl = 2NH_4Cl + CO_2$$

Lime is reconverted into chalk by sal volatile and liberates ammonia from it.

$(NH_4)_2CO_3$	+	$Ca(OH)_2$	=	$2NH_3$	+	$CaCO_3$	+	$2H_2O$	
Ammonium carbonate		Slaked lime		Ammonia		Chalk		Water	
$(NH_3)_2CO_2$	+	$Ca(OH)_2$	=	$2NH_3$	+	$CaCO_3$	+	H_2O	
Ammonium carbamate		Slaked lime		Ammonia		Chalk		Water	

CHAPTER VII

THE BURNING OF CHARCOAL AND THE COMPOSITION OF FIXED AIR

The Study of Gases.

The preceding chapters have shown how many of the fundamental facts of chemistry were disclosed by the study of salts, metals, and inflammable substances. A new era of rapid development dawned when the study of gases was added to that of the liquids and solids which had been the sole subjects of investigation throughout the alchemistic period. At how late a period this study began is disclosed by the dates when names were first assigned to various gases as they were differentiated clearly from common air.* Thus we have—

FIXED AIR	(Black, 1755),
INFLAMMABLE AIR	(Cavendish, 1766),
NITROUS AIR	(Priestley, 1772).

Oxygen and chlorine were not discovered until 1774, and did not receive these names until 1783 and 1810 respectively. The first step in the manipulation of gases was the use of a flask or jar inverted over water as a means of collecting and storing these elusive and intangible " airs " ; this device was used incidentally by Boyle in 1660, and systematically a few years later by Mayow. Apparatus for manipulating gases was described by Stephen Hales in 1727 in the course of a botanical investigation ; but full success was only attained in the hands of Cavendish and Priestley many years later Whilst, therefore, fixed air was recognised as a distinct chemical substance by Black in 1755, it was left to Cavendish, in 1766, to collect and examine the gas systematically, as described in the closing paragraph of the preceding chapter.

As illustrating the important results that followed from the successful manipulation of gases, the present chapter describes the investigation of the gaseous products formed by the burning of charcoal, and the discovery of the composition of " fixed air." The next chapter deals with the combustion of " inflammable air " and is followed in a further chapter by an account of the combustion of organic compounds

* Van Helmont (1577-1644), to whom we owe the name GAS, recognised the existence of a poisonous GAS SYLVESTRE and of an inflammable GAS PINGUE ; but these were merely vague types, like the " choke-damp " and " fire-damp " of miners, and not individual gases.

Fixed Air as a Product of Combustion.

Black found in 1757 that fixed air could be produced :—

(i) *By breathing*; air blown through lime-water rendered it cloudy.

(ii) *By fermentation.*

(iii) *By the burning of charcoal*; a piece of red-hot charcoal placed in the nozzle of a bellows imparted to the air blown through it the power of reconverting lime to chalk.

The production of fixed air by burning charcoal was also studied in 1772 by Priestley, who heated charcoal, by means of a burning mirror or lens, in air confined over water or mercury. When mercury was used, the charcoal burnt without producing any change of volume; but when lime-water was added it was rendered milky, and the volume of the air was diminished by one-fifth, on account of the absorption of fixed air produced by the combustion of the charcoal.

Fixed Air an Oxide.

Immediately after the discovery of oxygen, Lavoisier, in 1774, carried out an important experiment which proved that fixed air was an oxide. He heated the red calx of mercury, first with charcoal and then alone. In the former case fixed air was produced, in the latter case oxygen was set free; in both cases the mercury was recovered in the metallic state. On comparing the two equations :

$$\text{charcoal} + \text{mercury calx} = \text{mercury} + \text{fixed air},$$
$$\text{mercury calx} = \text{mercury} + \text{oxygen},$$

it is seen at once that the addition of charcoal on the left-hand side of the equation has converted the oxygen on the right-hand side into fixed air, so that, by subtraction we get

$$\text{charcoal} + \text{oxygen} = \text{fixed air}.$$

Lavoisier recognised that the burning of charcoal gave rise also to moisture and to considerable quantities of ash. It was therefore not correct to say that fixed air is an oxide of charcoal (French, *charbon*); it was really an oxide of an ideal charcoal, which he proposed to call **carbon** (French, *carbone*).

Fixed Air an Acid.

There is a marked analogy between the decomposition by heat of chalk and of green vitriol. Thus :—

$$\text{chalk} = \text{lime} + \text{fixed air},$$
$$\text{green vitriol} = \text{rouge} + \text{oil of vitriol}$$

In each case a volatile product escapes and a fixed, earthy residue is left behind; but whereas the green vitriol gives rise to a strong acid, the gas which escapes from the chalk does not possess any marked acid properties. Its acid character was first recognised in 1774 by Bergman,

who called it the AERIAL ACID. In support of this view, Bergman mentions :—

(i) The fresh, almost acid, taste which fixed air imparts to natural and artificial aerated waters.

(ii) The fact that fixed air will redden tincture of litmus and the extract of blue cornflowers, although it does not produce any change in the less sensitive syrup of violets.

(iii) Its power of dissolving metals, especially iron and zinc.

(iv) The property which it possesses of rendering chalk and magnesite soluble in water.

As fixed air was produced from carbon in much the same way as sulphuric acid was produced from sulphur, and phosphoric acid from phosphorus, Lavoisier and his colleagues, in 1787, gave to fixed air the name **carbonic acid.** But, as Bergman recognised, the acid properties belong to the solution rather than to the gas; for this reason the name carbonic acid has now been transferred to the solution, whilst the gas itself is described as **carbonic anhydride**; it is also known as carbon dioxide.

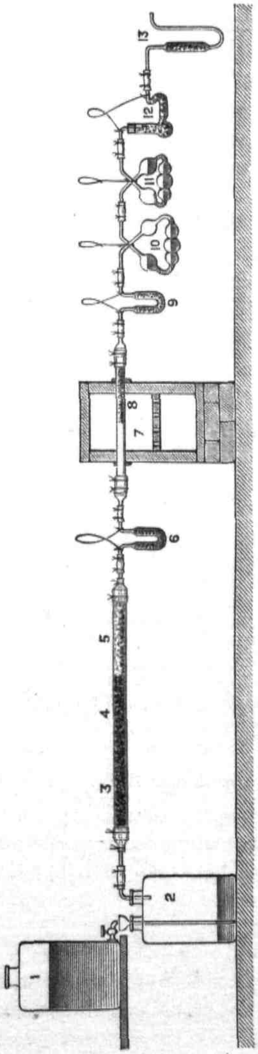


FIG. 44.—DUMAS AND STAS' APPARATUS FOR THE COMBUSTION OF GRAPHITE AND OF DIAMONDS.

1, Alkaline water; 2, Oxygen; 3, Alkaline pumice; 4, Fragments of potash; 5, Sulphuric acid; 6, Acid pumice; 7, Platinum boat; 8, Oxidised copper turnings; 9, Acid pumice; 10 and 11, Liebig apparatus; 12, Alkaline pumice and powdered potash; 13, Aspirator protected by potash.

The Composition of Fixed Air.

(*a*) Berzelius and Dulong in 1820 determined the composition of fixed air by taking advantage of the fact, which Priestley had discovered, that charcoal burns in air without producing any marked change of volume. Thus since

$$\text{carbon} + \text{oxygen} = \text{carbonic anhydride}$$
$$1\ vol. \qquad\qquad 1\ vol.$$

and the densities of the two gases relatively to air were 1·1026 and 1·524 respectively, it was evident that 1·524 parts of carbonic anhydride contained 1·1026 parts of oxygen and $1{\cdot}524 - 1{\cdot}1026 = 0{\cdot}4214$ parts

of carbon. The percentage composition of carbonic anhydride was therefore :—

Oxygen	=	**72·35**	per cent.
Carbon	=	**27·65**	,,

(*b*) This method of analysis is faulty, because the volumes of oxygen and of carbonic anhydride are only approximately equal. A more exact analysis was made in 1841 by Dumas and Stas, who burnt a known weight of carbon in oxygen and weighed the carbonic anhydride which was produced. For this purpose they used :

(i) A natural graphite, purified by igniting with potash, extracting with acids, and heating in a current of chlorine-gas (p. 268).

(ii) Graphite, separated from cast iron and purified in the same way.

(iii) Diamonds, which were used mainly because purified graphite was so porous that it was difficult to weigh it free from condensed air and moisture.

The methods used to purify the oxygen and to collect and weigh the carbonic anhydride produced by combustion are indicated in Fig. 44. The results of the combustions were as follows :

TABLE 6.—COMBUSTION OF CARBON.

	Carbon.	*Carbonic anhydride.*	*Percentage of carbon.*
Natural graphite (five combustions)	5·679	20·832	27·26
Artificial graphite (four combustions)	5·115	18·754	27·27
Diamond (five combustions)	5·398	19·7885	27·28
		Mean =	27·27

The composition of carbonic anhydride was therefore :—

Oxygen	=	**72·73**	per cent.
Carbon	=	**27·27**	,,

Diamond and Graphite. Allotropic Forms of Carbon.

Charcoal is not the only substance which gives fixed air or carbonic anhydride when burnt. Lavoisier in 1772 showed that, when air was excluded, DIAMOND (which had been burnt by several earlier workers) remained unaltered at the highest temperature of the furnace. When, however, diamonds were heated, by means of a large burning-glass, in air or oxygen confined over mercury, combustion took place ; the formation of carbonic anhydride was proved by the diminution of volume and by the cloud of chalk which appeared when lime-water was introduced.

Tennant in 1797 burnt diamonds by means of fused saltpetre and showed that they gave rise to the same quantity of fixed air as when an equal weight of charcoal was burnt. In just the same way, Scheele in 1779 showed that the mineral GRAPHITE, also known as PLUMBAGO or BLACKLEAD, could be burnt to fixed air by fusing it with saltpetre.

It thus appeared that charcoal, graphite, and diamond all gave fixed air as the chief product of combustion. In spite of their widely different properties, each substance must be regarded as a more or less impure form of the ideal substance which Lavoisier had called "carbon" and which would give rise to nothing but fixed air when burnt. Such distinct varieties of an element as charcoal, graphite, and diamond were described by Berzelius in 1841 as ALLOTROPES (Greek ἄλλος, other; τροπός, direction).

SUMMARY AND SUPPLEMENT.

1. **Carbon and its Oxide.**—Carbon burnt in air over mercury gives rise to "fixed air" without change of volume (Priestley).

$$\underset{}{C} + \underset{1\ \text{vol.}}{O_2} = \underset{1\ \text{vol.}}{CO_2}$$

The composition of fixed air can therefore be deduced from its density relatively to oxygen (Berzelius and Dulong, 1820).

"Fixed air" is also produced when litharge or the red oxide of mercury is heated with charcoal to reproduce the metal (Lavoisier, 1774).

$$C + \underset{\text{Litharge}}{2PbO} = CO_2 + \underset{\text{Lead}}{2Pb}$$

$$C + \underset{\text{Mercuric oxide}}{2HgO} = CO_2 + \underset{\text{Mercury}}{2Hg}$$

Since mercuric oxide when heated alone gives mercury and oxygen,

$$2HgO = O_2 + 2Hg,$$

it follows that "fixed air" is an oxide. The ideal charcoal of which it is the oxide is described as **carbon** (Lavoisier, 1787).

2. **Carbonic Acid and the Carbonates.**—Bergman in 1774 recognised that fixed air when dissolved in water formed a weak acid. This acid is now called **carbonic acid** and the gas is called **carbonic anhydride** or **carbon dioxide.**

$$\underset{\text{Carbonic anhydride}}{CO_2} + \underset{\text{Water}}{H_2O} = \underset{\text{Carbonic acid}}{H_2CO_3}$$

The salts derived from it are called **carbonates,** *e.g.*,

Soda	Sodium carbonate,	Na_2CO_3
Potash	Potassium carbonate,	K_2CO_3
Magnesia	Magnesium carbonate,	$MgCO_3$
Chalk	Calcium carbonate,	$CaCO_3$

3. **Bicarbonates.**—When aqueous potash is exposed to air a less soluble salt crystallises out (Black, 1755), in which twice as much fixed air is combined with the alkali (Cavendish, 1766). This salt is **potassium bicarbonate,** $KHCO_3$.

Chalk and magnesia, on the other hand, dissolve in water containing "fixed air" (Cavendish, 1766) owing to the formation of a more soluble **magnesium bicarbonate**, $Mg(CO_3H)_2$, or **calcium bicarbonate**, $Ca(CO_3H)_2$.

$$MgCO_3 + H_2O + CO_2 = Mg(CO_3H)_2$$
$$CaCO_3 + H_2O + CO_2 = Ca(CO_3H)_2$$

Iron dissolves in carbonic acid (Bergman, 1774), and is present in chalybeate waters dissolved in an excess of carbonic acid (Lane, 1769), as **ferrous bicarbonate**, $Fe(CO_3H)_2$.

$$Fe + H_2CO_3 = FeCO_3 + H_2$$
$$FeCO_3 + H_2O + CO_2 = Fe(CO_3H)_2$$

These three compounds impart to water a TEMPORARY HARDNESS which can be removed by boiling off the fixed air, *e.g.*,

$$Ca(CO_3H)_2 = CaCO_3 + H_2O + CO_2$$

whilst soluble salts of magnesia and lime produce PERMANENT HARDNESS which can be removed by precipitation with a mild alkali (Cavendish, 1767).

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$
$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$

The bicarbonate of iron on exposure to oxygen liberates its fixed air and yields a yellow RUST of ferric hydroxide, $Fe(OH)_3$.

$$4Fe(CO_3H)_2 + 2H_2O + O_2 = 4Fe(OH)_3 + 8CO_2.$$

CHAPTER VIII

THE BURNING OF HYDROGEN AND THE COMPOSITION OF WATER

A.—The Burning of Hydrogen.

Artificial Gases.

Throughout the alchemistic period it was believed that air was an element, which might be contaminated with vapours of different kinds, but could not be altered in its fundamental properties. When, therefore, the gases produced by the action of acids on iron were collected by Boyle in 1660 and by Mayow in 1674 (Fig. 45), it was still uncertain whether the products differed in any essential way from common air. This uncertainty continued until Black in 1755 showed that fixed air could be distinguished from all other gases by its power of reconverting lime into chalk. Cavendish in 1766 showed that fixed air could also be identified by means of its density and its solubility in water. From whatever source the gas was prepared, it dissolved in its own volume of water and was found to be 1·57 times heavier than air and 511 times lighter than water.

Fig. 45.—Mayow's Apparatus for Collecting Artificial Gases.

The flask was filled with weak acid and inverted in a dish of the same acid; iron shot were pushed up into the neck of the flask and the gases thus set free were collected.

Cavendish applied similar methods to the gas obtained by the action of metals on acids, which he called INFLAMMABLE AIR. He found that this gas was seven times lighter than common air (the correct number is 14·4 times) and 5500 times (really 11,600 times) lighter than water. By measuring its density Cavendish proved that the same gas is formed by the action of:

(i) Zinc on oil of vitriol and on muriatic acid.
(ii) Iron on oil of vitriol.
(iii) Tin on muriatic acid.

He also showed that the volume of gas produced by the solution of a given weight of a metal was the same whichever acid was used and that the quantity of gas did not depend on the strength of the acid.

The Burning of Inflammable Air.

When Lavoisier had proved that sulphur and phosphorus united with oxygen to form acids, whilst charcoal also gave rise to a feeble acid when burnt, it was generally expected that the burning of inflammable air would yield an acid product of some sort. Many experiments were made to detect this acid. Lavoisier, for instance, in 1777 carried out the experiment of burning inflammable air in a flask containing lime-water, but found that no fixed air was produced. He repeated the experiment with distilled water, but this remained pure and gave no sign of acid. Diluted alkali was also not changed in any way by the burning of inflammable air in the flask.

It had long been known that water was produced by the burning of spirit of wine. Similar observations were soon made on inflammable air. Thus, Macquer in 1776 had obtained droplets of pure water by burning inflammable air in contact with a fragment of white porcelain. Again, Priestley, in 1781, noticed that dew was formed in a glass globe in which he had exploded a mixture of common air and inflammable air. No importance was attached to these observations because it was a common experience that moisture could be condensed out from air very easily by cooling; it might, therefore, be thrown out still more easily from air which had been altered profoundly by the process of combustion. Cavendish, however, in 1781 repeated Priestley's experiment, and became curious as to the real nature of the dew which was deposited when inflammable air and common air were exploded together in a glass globe. In order to examine this dew, Cavendish burnt seven gallons of inflammable air with 2½ times that quantity of common air. The gases were led through separate copper pipes to the end of a glass tube 8 feet long and ¾ inch in diameter, where they were burnt together. At the end of the experiment 135 grains of water had condensed in the tube. The water had no taste or smell and left no sediment when evaporated; the product appeared in fact to be pure water.

Water an Oxide.

For nearly two thousand years, water had been regarded as an element. Cavendish's experiment showed that it was really a compound formed by the union of inflammable air with common air. The explosion of inflammable air with pure oxygen should have settled the composition of water finally; but when this experiment was carried out, Cavendish no longer obtained pure water as the product, but a dilute solution of nitric acid; 30 grains of the watery product, when neutralised with potash, yielded 2 grains of crystals of ordinary saltpetre. Three years of work were required to prove that this nitric acid had been formed by the oxidation of azote, or nitrogen, present as an impurity in the exploding gases, and it was not until 1784 that Caven-

dish felt free to publish his experiments. Their significance had already been realised by Lavoisier, who, in 1783, having heard of them privately, burnt a mixture of inflammable air and oxygen in a bell-jar inverted over mercury and obtained half an ounce of pure water. Whilst Cavendish was still uncertain as to the part played by fire or phlogiston in the composition of water, Lavoisier was able to conclude at once that water was a compound of inflammable air with oxygen in which phlogiston played no part whatever. He therefore suggested, in 1787, that inflammable air should be described as HYDROGEN or "water producer" (Greek ὕδωρ, water, and γεννάω, I beget; compare German, *Wasserstoff*), since his experiments had proved that water was "nothing but oxygenated hydrogen, or the immediate product of the combustion of oxygen gas with hydrogen gas."

Lavoisier decomposes Water by Means of Iron.

Having shown that water was a compound of inflammable air with oxygen, Lavoisier argued that it should be possible to reproduce this inflammable air by removing oxygen from water with the help of some easily oxidised substance. He succeeded in doing this by passing steam through an iron gun-barrel heated in a charcoal furnace (Fig. 46). When the gun-barrel was red hot, water was allowed to flow into it drop by drop. The iron gun-barrel was oxidised rapidly, until at the end of the experiment it was completely converted into the black magnetic oxide of iron. The hydrogen set free from the water was collected in an inverted bell-jar, whilst the part of the water which escaped decomposition (especially towards the end of the experiment) was condensed in a spiral "worm," as shown in the figure.

Lavoisier repeated this experiment with a copper pipe in place of the iron gun-barrel; but the affinity of this metal for oxygen is so much less than in the case of iron that the whole of the water which passed into the tube was condensed again in the worm, without producing any corrosion of the copper or liberation of inflammable air.

Hydrogen as a Reducing Agent. Oxidation and Reduction.

Priestley had found in 1785 that red lead could be "revivified" by heating it in an atmosphere of hydrogen. Lavoisier showed that in this experiment the hydrogen was oxidised to water so that—

red lead + hydrogen = lead + water.

Similar changes are produced by heating the oxides of copper and of iron with hydrogen, thus:

oxide of copper + hydrogen = copper + water
oxide of iron + hydrogen = iron + water;

but the refractory oxide of zinc is not acted upon by the gas. The

process of taking away oxygen is now generally described as REDUCTION, but this word is also used to describe changes in which hydrogen or a metal is added to a substance, or an acid radical removed from it.

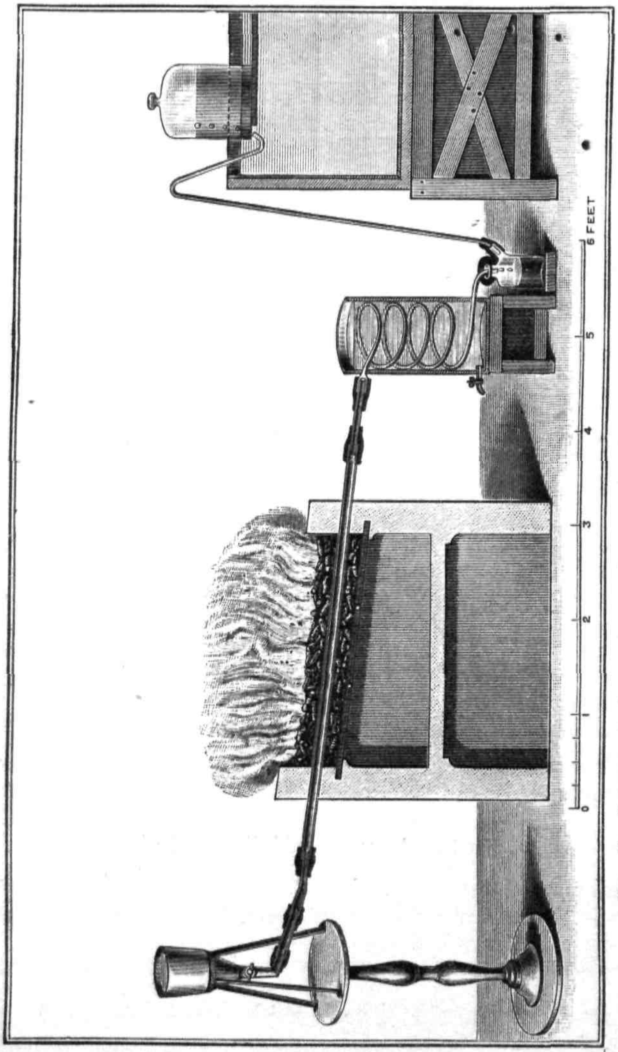


FIG. 46.—LAVOISIER'S APPARATUS FOR DECOMPOSING STEAM IN A RED-HOT GUN-BARREL.

In the same way, the term OXIDATION is often used to describe, not only the addition of oxygen, but the removal of hydrogen or a metal, or the addition of an acid radical.

Decomposition of Steam by Iron as a Balanced Action.

In the case of iron, oxidation and reduction may both take place as shown by the two arrows in the equation

$$\text{oxide of iron} + \text{hydrogen} \rightleftarrows \text{iron} + \text{steam}.$$

Thus when oxide of iron is heated in hydrogen, the oxide is reduced and steam is formed; but the action stops when the gases contain a definite proportion of hydrogen and steam, which varies with the temperature at which the experiment is made (see p. 779). Conversely, when iron is heated in steam, the iron is oxidised and hydrogen is set free; but this action stops also when the gases contain the same proportion of hydrogen and steam. This type of action, which proceeds up to a certain point and then stops before it is complete, is described as a BALANCED ACTION.

The LAW OF MASS ACTION states that the products of the ACTIVE MASS of the components on the two sides of a balanced equation are in a constant ratio, *e.g.*, if the active masses are

$$\underset{C_1}{\text{oxide of iron}} + \underset{C_2}{\text{hydrogen}} \rightleftarrows \underset{C_3}{\text{iron}} + \underset{C_4}{\text{steam}}$$

then

$$C_1 \times C_2 = K \times C_3 \times C_4.$$

The "active masses" of the components of a gaseous or liquid mixture are usually proportional to their concentrations, whilst the "active mass" of a solid at a given temperature is taken as a constant. At any given temperature, therefore, C_1 and C_3 in the preceding equation are constants, and the variables C_2 and C_4 will be in a fixed ratio

$$\frac{\text{steam}}{\text{hydrogen}} = \frac{C_4}{C_2} = \frac{1}{K}\frac{C_1}{C_3} = \text{constant}$$

$$= \text{about } 0{\cdot}2 \text{ at } 400^\circ$$

$$\text{or about } 1 \text{ at } 1000^\circ.$$

A balanced action can be brought to completion by using an excess of one of the gaseous (or liquid) components, *e.g.*, the reduction of oxide of iron is complete in a current of hydrogen, which sweeps away the steam as fast as it is formed; and the oxidation of iron can be carried to completion in a current of steam, which sweeps away the hydrogen as fast as it is formed.

B.—QUANTITATIVE EXPERIMENTS ON THE COMPOSITION OF WATER.

Early Volumetric Experiments.

The volumetric composition of water was established by Cavendish in the experiments in which he first showed that water is a compound of hydrogen and oxygen. He found that 423 measures of hydrogen were just sufficient to remove the oxygen from 1000 measures of air. If we assume that 20·9 per cent. of the atmosphere consists of oxygen, this would mean that 209 measures of oxygen combine with 423 measures

of hydrogen. Direct experiments on the explosion together of hydrogen and oxygen showed that the combining volumes were almost exactly 1 volume of oxygen to 2 volumes of hydrogen. More exact measurements made by Gay-Lussac and Humboldt in 1805 showed that 100 parts of oxygen united with 199·89 parts of hydrogen; these numbers again did not differ appreciably from the exact ratio 1 : 2.

Attempts were made to deduce the gravimetric composition of water by combining these numbers with measurements of the densities of the two gases; but the values for the density of hydrogen were so inexact that the ratio by weight was found to be only 4 or 5 instead of 8 parts of oxygen to one of hydrogen. It should be noticed, however, that the exact experiments of Morley (p. 90) were based upon a return to this earliest method of determining the composition of water.

Gravimetric Experiments on the Composition of Water.

In 1820, three gravimetric experiments on the composition of water were made by Berzelius and Dulong. Instead of combining the two gases directly, they passed hydrogen over copper oxide, thereby producing water and metallic copper, thus:

$$\text{hydrogen} + \text{copper oxide} = \text{water} + \text{copper}.$$

No attempt was made to weigh the gases directly, but the water was weighed, and the weight of oxygen which it contained was calculated from the loss in weight of the copper oxide. The difference between the weights of the water and of the oxygen gave the weight of the hydrogen.

Berzelius and Dulong as a mean value from their three experiments obtained the ratio :—

$$\textit{oxygen} : \textit{hydrogen} = 88{\cdot}9 : 11{\cdot}1 = \mathbf{8{\cdot}01 : 1}$$

Dumas's Experiments on the Composition of Water.

These experiments were repeated on a very large scale by Dumas in 1842. The hydrogen, prepared by the action of zinc on diluted sulphuric acid, was purified and dried by passing it through seven U-tubes each about a metre in height (Fig. 47): these contained lead nitrate solution to remove *sulphuretted hydrogen*; silver nitrate solution to remove *arseniuretted hydrogen*; potash to remove *acid vapours*; and oil of vitriol cooled in ice, or phosphoric oxide, to remove *water vapour*. The copper oxide and copper were weighed in a large vacuous bulb provided with a beak 1 metre in length; during the reduction, the bulb was heated by a large spirit lamp. The water was condensed in a glass bulb and the vapour absorbed in U-tubes similar to those used for drying the hydrogen. In nineteen experiments Dumas prepared one kilogram of water and found the ratio :—

$$\textit{oxygen} : \textit{hydrogen} = \mathbf{7{\cdot}98 : 1}$$

Scott's Experiments on the Composition of Water.

Dumas' figures for the composition of water remained unchallenged for half a century till Scott in 1893 obtained an independent value by

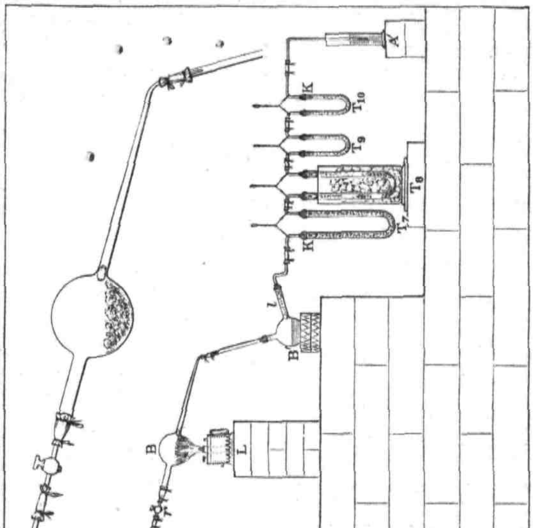


FIG. 47.—DUMAS' APPARATUS FOR DETERMINING THE COMPOSITION OF WATER.

The inset shows the copper oxide bulb on a larger scale. The details of the apparatus are as follows:—F, Flask for generating hydrogen; E, Tap-funnel containing sulphuric acid; A, Safety-valve of mercury; T_1, Tube containing glass moistened with lead nitrate; T_2, Tube containing glass moistened with silver sulphate; T_3, Tube containing (*a*) alkaline pumice, (*b*) solid potash; T_4T_4, Ignited potash, broken; T_5T_5, Tubes containing pumice coated with phosphoric anhydride and cooled with a freezing mixture; T_6, Guard tube containing pumice and phosphoric anhydride; B, Bulb containing copper oxide, with tap *r* above, and pointed beak below to carry off water; L, Spirit lamp; B′, Receiver for water, with fragments of calcium chloride at *l*; T_7, Ignited potash; T_8, Phosphoric anhydride in a freezing mixture; T_9, Guard tube containing phosphoric anhydride; T_{10}, Phosphoric anhydride (not weighed) to exclude moisture; A′, Valve containing sulphuric acid, for escape of hydrogen.

combining Lord Rayleigh's measurements of the densities of hydrogen and oxygen with his own measurements of the combining volumes. The hydrogen used in these experiments was prepared by the action of

sodium on steam (p. 557), with or without absorption by palladium (p. 91). The oxygen was prepared by heating silver oxide, mixed with a little caustic potash in case the oxide should be contaminated with carbonate and thus liberate traces of carbonic anhydride. Both gases were of the highest degree of purity, the residue left after explosion being usually less than one part in 100,000.

By combining the ratio of the densities, 15·882 : 1, with the ratio of the combining volumes, 2·00245 : 1, the combining weights of the gases were found to be

$$\textit{oxygen} : \textit{hydrogen} = \mathbf{7{\cdot}931 : 1}.$$

Morley's Experiments on the Comipostion of Water.

A still more exact determination of the composition of water was made on similar lines by E. W. Morley in 1895.

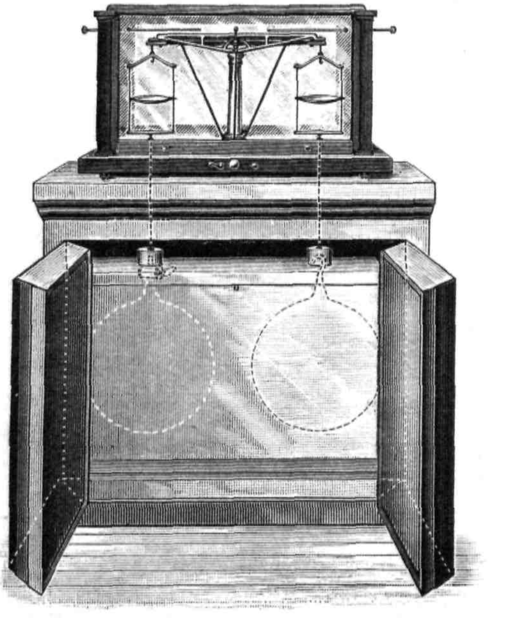


FIG. 48.—MORLEY'S APPARATUS FOR DETERMINING THE DENSITY OF OXYGEN.

In these experiments the use of copper oxide was again discarded; the hydrogen and oxygen were weighed directly, as in the earliest experiments, but with all the added resources which had accrued from the experimental work of the intervening century.

(*a*) The *density of oxygen* (prepared by heating potassium chlorate or by electrolysing dilute sulphuric acid) was determined by weighing it directly in globes of 20 litres capacity, suspended in pairs in a large desiccator-cupboard from the pans of a balance (Fig. 48). In a typical experiment the data were:

Volume	21568·4 c.c.	Weight	28·4308 grams.
Temperature	17·48°	Corrected	17·40°.
Barometer	745·91 mm.	Corrected	746·29 mm.

Weight of 1 litre of oxygen at sea level in 45° latitude, at 0° and 760 mm. pressure . . . 1·42883 grams.

The mean of three complete series of experiments, in which different methods were used for measuring temperature and pressure, gave the value

density of oxygen = **1·42900** ± 0·000034.

(*b*) The *density of hydrogen* was determined in a different way, both on account of the difficulty of weighing 1·8 grams of gas in a globe 600 times heavier, and also because of the risk that this small weight might be increased appreciably by the presence of mercury vapour. In the final series of experiments, therefore, the gas was weighed in a tube containing 600 grams of metallic palladium (Fig. 49); this absorbed 3·8 grams of hydrogen, and on heating the tube 3·7 grams or about 40 litres of pure hydrogen were expelled into three large globes

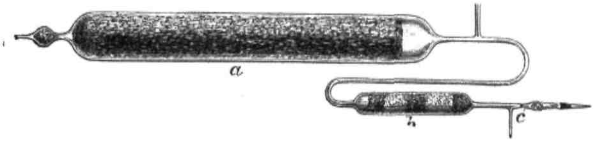


FIG. 49.—MORLEY'S PALLADIUM-TUBE FOR WEIGHING HYDROGEN.
a is a bulb containing 600 grams of palladium; *b* contains phosphoric anhydride to dry the gas; *c* is a seal of fusible metal.

immersed in ice; the pressure produced in these globes by a known weight of gas was measured. In a typical experiment the data were:

Volume of three globes . . .	43·2574 litres
,, ,, air space in manometer . .	0·0536 ,,
,, ,, leads	0·0365 ,,
Temperature, 0°. Total volume . .	43·3475 litres.
Pressure (corr.) 725·30 mm.	Weight = 3·7158 grams.
Density of hydrogen . . .	0·089864 gram per litre.

Twenty-five experiments made in this way gave an average value

density of hydrogen = **0·089873** ± 0·0000027.

(*c*) In order to find the weights of the gases which combine together to form water, it was necessary next to determine the ratio of their *combining volumes*. For this purpose Morley prepared a mixture of the two gases by passing an electric current through dilute potash cooled in ice. The apparatus was provided with drying tubes and a tap and was arranged so that it could be weighed before and after delivering the gas. The density of the gas was determined in the same way as in the case of hydrogen, by finding the pressure produced in the three large globes by a known weight of the gas. In a typical experiment 23·0269 grams of the gas produced a pressure of 753·97 mm. in a volume of 43·3628 litres; density 0·535513; mean of ten experiments 0·535510 ± 0·000010. From this density the proportion of hydrogen to oxygen was calculated, after making various corrections, to be 2·00357. By

exploding the gas in a eudiometer, it was found that there was a slight excess of hydrogen, amounting to 0·000293 of the total volume or 0·00088 of the volume of the oxygen. The combining volumes were therefore in the proportion

$$hydrogen : oxygen = 2{\cdot}00269 : 1.$$

(*d*) A second method of determining the composition of water was by weighing the water produced by the combination of known weights of hydrogen and oxygen. The hydrogen (21 litres) was drawn from a palladium tube, *a* (Fig. 49), provided with a drying tube of phosphoric anhydride, *b*, and a tiny plug of fusible metal, *c*, in place of a tap. The oxygen (42 litres) was drawn from two large globes which were weighed in the same way as in the density experiments. The combustion was carried out in a cylindrical glass tube (Fig. 50) provided with two jets, *aa*, and a pair of wires, *ff*, for a spark to ignite the gas. During the combustion the upper part of the tube was surrounded with cold water and the lower part with a freezing-mixture (Fig. 51). The tube was exhausted before and after the combustion; the water produced was frozen before exhausting, and drying tubes, *bb*, were provided on either side in order that none of the water might be lost. The gas remaining in the chamber at the end of the experiment was collected and analysed. In a typical experiment the weights were:

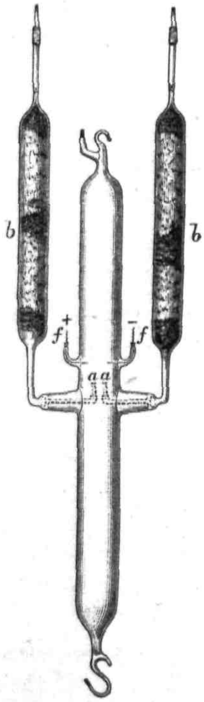


FIG. 50.—MORLEY'S COMBUSTION-TUBE.

The gases were admitted by jets *aa* after passing through drying tubes *bb*; they were ignited by sparking at *ff*.

Hydrogen .	3·8223 — 0·0012 =	3·8211 grams
Oxygen .	30·3775 — 0·0346 =	30·3429 ,,
Total		34·1640 ,,
Water	=	34·1559 ,,

Whence

oxygen to hydrogen . . = 7·941
water to hydrogen . . = 8·939

(*e*) The mean of twelve experiments in which 400 grams of water were produced, as in (*d*), gave the ratios:

(i) *water* to *hydrogen* = 8·9392 : 1
or *oxygen* to *hydrogen* = **7·9392 : 1**
(ii) *oxygen* to *hydrogen* = **7·9396 : 1**

From the ratio 15·9002 of the densities and 2·00269 of the combining volumes the two constituents are in the ratio

(iii) *oxygen* : *hydrogen* = **7·9395** : 1.

The general mean is therefore

oxygen : *hydrogen* = **7·9394** : 1.

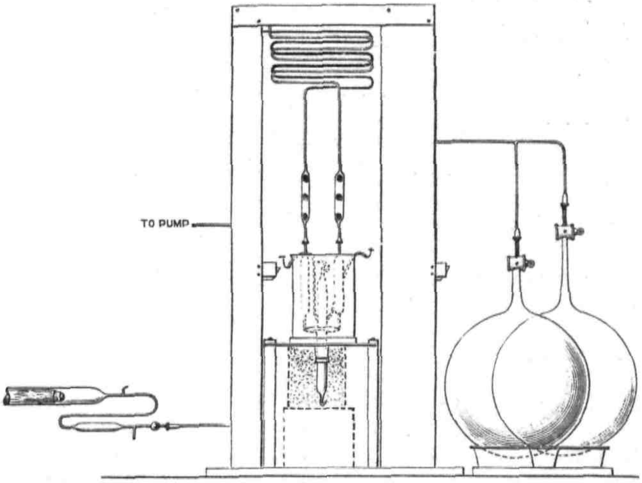


FIG. 51.—MORLEY'S APPARATUS FOR THE COMBUSTION OF HYDROGEN AND OXYGEN.

The leads for the hydrogen (on the left) and for the oxygen (on the right), with the regulating taps, are hidden behind the wooden frame. They are joined to the combustion tube by long, flexible, glass leads, terminating in drying tubes. The upper part of the combustion-chamber is surrounded by water, the lower part by a freezing-mixture.

SUMMARY AND SUPPLEMENT.

1. **Water an Oxide.**—When "inflammable air" (Cavendish, 1766), produced by the action of metals on acids, is burnt in air or oxygen pure water is produced (Cavendish, 1781),

$$2H_2 + O_2 = 2H_2O;$$

the inflammable gas was therefore described by Lavoisier in 1787 as HYDROGEN.

2. **Oxidation and Reduction.**—Hydrogen can be separated from steam by the action of red-hot iron (Lavoisier, 1784). The action is, however, reversible, since the blue-black oxide of iron can be reduced by means of hydrogen (Priestley),

$$3Fe + 4H_2O \underset{\text{Reduction}}{\overset{\text{Oxidation}}{\rightleftarrows}} Fe_3O_4 + 4H_2.$$

Copper oxide and litharge are also reduced by hydrogen, but are not produced by the action of steam on the metals; conversely, zinc oxide and

magnesia are not reduced by hydrogen, but are produced by the action of steam on the metals.

$$CuO + H_2 \longrightarrow Cu + H_2O$$
$$PbO + H_2 \longrightarrow Pb + H_2O$$
$$ZnO + H_2 \longleftarrow Zn + H_2O$$
$$MgO + H_2 \longleftarrow Mg + H_2O$$

3. **Balanced Actions.**—The action of steam on iron is a good example of a BALANCED ACTION. The equilibrium between the direct and the reversed change is determined by the ACTIVE MASS of the materials on the two sides of the equation. Thus if the active masses of the components on the left-hand side of the equation are C_1, C_2 . . . C_x, and of those on the right-hand side are C'_1, C'_2 . . . C'_y, then the LAW OF MASS ACTION states that *the products of these numbers must be in a constant ratio* K, as shown in the general formula

$$C_1 \times C_2 \times C_3 \times \ldots \times C_x = KC'_1 \times C'_2 \times \ldots \times C'_y.$$

The active mass of a solid is taken as a constant for each temperature, whilst that of a gas or liquid is usually proportional to its partial pressure or concentration. Since the chemical equation, as given on the preceding page, involves 3 atoms of iron, and 4 molecules of steam and of hydrogen, the conditions of equilibrium are

$$C^3_{Fe} \times C^4_{H_2O} = KC_{Fe_3O_4} \times C^4_{H_2}$$

or, since C_{Fe} and $C_{Fe_3O_4}$ are constants,

$$C_{H_2O} = K^1 \times C_{H_2}.$$

where C_{H_2O} and C_{H_2} are the concentrations or partial pressures of steam and hydrogen and K^1 is a constant. The values of the ratio C_{H_2O}/C_{H_2} for the two successive stages of the action Fe $\rightleftharpoons$ FeO $\rightleftharpoons$ Fe_3O_4 are as follows :—

Temperature	400°	500°	600°	700°	800°	850°
First stage ($Fe + H_2O \rightleftharpoons FeO + H_2$)						
$K_1 = C_{H_2O}/C_{H_2}$ . . .	0·15	0·23	0·33	0·46	0·61	0·70
Second stage ($3FeO + H_2O \rightleftharpoons Fe_3O_4 + H_2$)						
$K_2 = C_{H_2O}/C_{H_2}$ . . .	0·20	0·32	0·52	0·85	1·35	1·85

4. **Composition of Water.**—The composition of water has been determined

(*a*) *By direct synthesis*

$$2H_2 + O_2 = 2H_2O.$$

This usually involves measurements of the densities and combining volumes of the two gases (Scott, 1893) ; but Morley in 1895 also carried out a direct gravimetric synthesis, weighing both gases and the water produced from them. The combining volumes at 0° at 760 mm. are in the ratio

$$\textit{hydrogen} : \textit{oxygen} = 2{\cdot}0027 : 1$$

and the combining weights are in the ratio

$$\textit{oxygen} : \textit{hydrogen} = 7{\cdot}9394 : 1.$$

(*b*) *By reduction of copper oxide,*

$$CuO + H_2 = Cu + H_2O$$

(Berzelius and Dulong, 1820, Dumas, 1842). In this method the water is collected and weighed, and the weight of oxygen determined by weighing the copper oxide in an exhausted bulb before and after reducing it to copper. The weight of hydrogen is determined by difference.

CHAPTER IX

THE BURNING OF INFLAMMABLE GASES, LIQUIDS, AND SOLIDS

A.—Carbonic Oxide.

Water and Carbonic Anhydride as Products of Combustion.

The formation of fixed air and of water as products of the combustion of organic materials had been known vaguely from the time of Van Helmont (1577–1644); but it was only when Black had identified "fixed air" by its power of reconverting lime into chalk that this gas could be detected with certainty as a product of combustion. When Lavoisier, nearly twenty years later, in 1774, proved that fixed air was an oxide of carbon (p. 78), the production of fixed air on combustion became the most obvious test for the presence of carbon in an inflammable compound. In nearly every case water was also produced; but, whilst hydrogen was the only substance which gave water as the *only* product of combustion, there were three different substances, pure charcoal, pure graphite, and diamond, which gave nothing but fixed air or carbonic anhydride; to these three allotropic forms of carbon there must be added the inflammable oxide of carbon which is described in the following paragraph.

Lassone (1776) prepares an Inflammable Gas by Reducing Oxide of Zinc with Charcoal.

When charcoal is burnt in air or oxygen, or with the help of an easily reduced oxide such as red lead or copper oxide, it is oxidised at once to carbonic anhydride. There are, however, a few refractory oxides, such as oxide of zinc, which can be reduced with charcoal, but are not capable of oxidising the charcoal completely to carbonic anhydride. Lassone, in 1776, found that when the white calx of zinc was heated with a quarter of its weight of charcoal in an iron barrel, it yielded a large volume of a gas which burnt with a "very beautiful blue flame" and differed from hydrogen in that it could not easily be made to detonate when mixed with air or oxygen. This gas is an oxide of carbon and is now known as CARBONIC OXIDE.

Carbonic Oxide prepared by Reducing Carbonic Anhydride.

Although they were not able to burn carbon directly to carbonic oxide, Désormes and Clément showed in 1801 that the inflammable oxide could be prepared by reducing carbonic anhydride by passing it over red-hot charcoal. The fully burnt gas (carbonic anhydride) then shares its oxygen with a further quantity of charcoal, giving rise to carbonic oxide; but when this is burnt carbonic anhydride is again produced. The chemical changes which take place may be shown by the three equations:—

(i) carbon + oxygen = carbonic anhydride.
(ii) carbonic anhydride + carbon = carbonic oxide.
(iii) carbonic oxide + oxygen = carbonic anhydride.

These changes are constantly taking place in an ordinary coal fire where carbonic anhydride is formed first, but is reduced by the red-hot fuel to carbonic oxide, which may be seen burning at the top of the fire with a lambent blue flame. The same process may also be carried out in an enclosed furnace, in such a way that the inflammable gas formed in the upper layers of the fire can be used for heating furnaces or for driving gas-engines. The gas prepared in this way is known as PRODUCER-GAS (Fig. 180, p. 467), and consists mainly of carbonic oxide and nitrogen.

Carbonic Oxide formed by the Action of Steam on Charcoal.

Amongst the refractory oxides, which may be used to convert carbon to carbonic oxide, water-vapour must be included. Désormes and Clément showed that, when steam is passed over red-hot charcoal, the hydrogen is liberated, whilst the oxygen is converted into carbonic oxide, thus:

steam + charcoal = hydrogen + carbonic oxide.

This mixture of gases is now produced industrially, under the name of WATER-GAS, by blowing steam into fuel which has been made hot by an air blast. As the steam cools the fuel, water gas can only be prepared alternately with producer gas, which has a much lower quality since it is diluted with large volumes of nitrogen. A mixture prepared by blowing air and steam together into fuel is known as SEMI-WATER GAS.

Carbonic Oxide prepared by Reducing Carbonates.

Carbonic oxide can also be prepared by reducing the carbonic anhydride of carbonates by means of charcoal or iron. Cruikshank in 1801 found that many gallons of the gas could be prepared by heating chalk with iron plates. Another carbonate, used both by Cruikshank and by Désormes and Clément, was the carbonate of baryta. This is found, *e.g.*, in Northumberland, as a heavy mineral to which the name of WITHERITE is given. It is shown to be a carbonate by its effervescence with acids; but, unlike chalk, it cannot be decomposed

by heating it in a common kiln or furnace. The very firmly fixed air which it contains can, however, be eliminated by the reducing action of charcoal, when it escapes in an inflammable form as carbonic oxide (Désormes and Clément). The earth which remains behind is very similar to quicklime and is known as BARYTA.

Cruikshank found that a very pure gas was formed by heating the "carbonated baryta" with iron plates. These could both be heated until completely dry; they had the advantage of giving a gas which was quite free from hydrogen—an impurity which was always present when the gas was prepared with the help of charcoal.

Composition of Carbonic Oxide.

The inflammable gas prepared in these different ways was shown both by Cruikshank and by Désormes and Clément to give nothing but carbonic anhydride when burnt. But when they measured the volume of oxygen which was used they found that only half the oxygen of the carbonic anhydride had been accounted for. The other half must have been present in the inflammable gas, which was therefore described as a "gaseous oxide of carbon."

More accurate experiments, carried out a few years later by Berthollet, showed that—

$$\underset{1\ vol.}{\text{carbonic oxide}} + \underset{\frac{1}{2}\ vol.}{\text{oxygen}} = \underset{1\ vol.}{\text{carbonic anhydride}}$$

Since carbonic anhydride contains its own volume of oxygen, carbonic oxide, which requires a second half-volume of oxygen for its complete combustion, may be regarded as half-burnt carbon.

The Gravimetric Composition of Carbonic Oxide.

In 1849, Stas carried out an analysis of carbonic oxide, in which 128·367 grams of oxygen were used in eight experiments to burn 224·683 grams of the gas to 353·050 grams of carbonic anhydride. The experimental methods were very similar to those used by Dumas to determine the composition of water. Thus, instead of using free oxygen to burn the gas, the oxygen was supplied by copper oxide, which was reduced to copper by heating it in a current of carbonic oxide. The gas was not weighed directly: its weight was calculated from the difference between the weight of oxygen used and the weight of carbonic anhydride produced. The carbonic anhydride was absorbed and weighed in combination with potash.

The chief difficulty of the experiment was to provide a supply of carbonic oxide free from carbonic anhydride, oxygen, water, hydrogen, and other inflammable gases. The gas was prepared by heating oxalic acid with oil of vitriol: the product, a mixture of carbonic oxide and carbonic anhydride, was passed through potash into a reservoir holding 80 to 90 litres (Fig. 52). From this reservoir the gas was displaced, not

by water, but by an alkaline solution capable of absorbing both oxygen and carbonic anhydride.* The chief means of removing oxygen consisted, however, in passing the carbonic oxide through a heated tube containing copper, in which the free oxygen would have every opportunity of being converted into carbonic anhydride. Both before and after passing through this tube the gas was freed from carbonic anhydride and from water by contact with potash and sulphuric acid. The gas prepared in this way contained a little nitrogen, but was practically free from all other impurities.

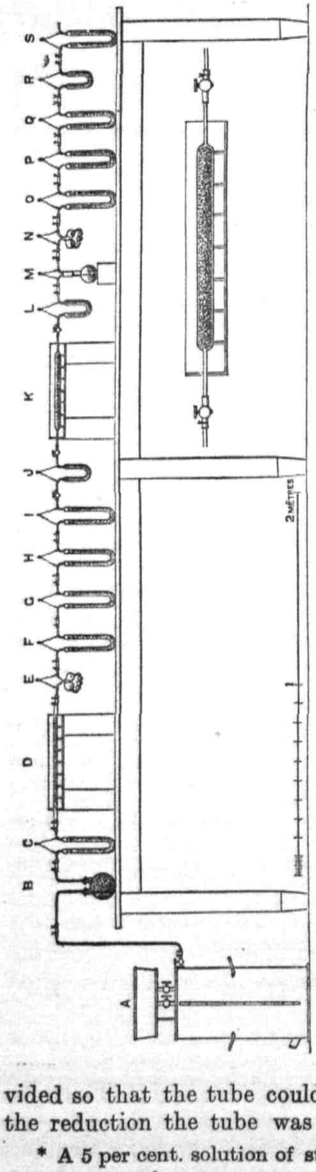


FIG. 52.—STAS'S APPARATUS FOR THE COMBUSTION OF CARBONIC OXIDE.

A, Gasometer (80–90 litres) containing carbonic oxide over an alkaline solution of stannous chloride; B, Potash on pumice; C, Sulphuric acid on pumice; D, Glass tube containing hot copper turnings; E, Aqueous potash; F, G, Potash on pumice; H, Powdered potash; I, Sulphuric acid on pumice; J, Guard-tube (with taps) containing sulphuric acid on pumice (weighed); K, Glass tube (50 cm. long, 2½ cm. diameter) containing copper oxide (weighed); L, Drying tube (weighed); M, Aqueous potash in bulb (weighed); N, Liebig potash-bulbs (weighed); O, Potash on pumice (weighed); P, (*a*) Potash on pumice, (*b*) Fused potash in powder (weighed); Q, Sulphuric acid on pumice (weighed); R, Guard-tube containing sulphuric acid on pumice (weighed); S, Sulphuric acid on pumice to exclude moisture from air. The glass tube, K, is shown on a larger scale as an inset.

In these experiments, as in those of Dumas and of Dumas and Stas, the purifying agents were distributed over pumice stone or broken glass, or were used in a granular form in order to secure ample contact with the gas. The air in the pumice stone was removed by exhausting the apparatus repeatedly and filling it again with pure carbonic oxide.

The copper oxide, prepared by calcination, was contained in a glass tube drawn out at each end. Taps were provided so that the tube could be exhausted before weighing. During the reduction the tube was heated quite gently over charcoal. In

* A 5 per cent. solution of stannous chloride in potash, made with boiled water, was used.

a series of blank experiments the tube was found to vary in weight by only a milligram on a total of 540 grams when heated, provided that some hours were allowed to elapse before reweighing.

The gas escaping from the copper oxide tube was passed through sulphuric acid to absorb any water that might be formed; the quantity collected was usually about 10 milligrams. It then passed into a bulb containing potash, where most of the carbonic anhydride was absorbed. A set of Liebig bulbs filled with potash and three U-tubes, the last filled with solid potash,* were used to absorb the remainder of the gas. The weight of carbonic anhydride must be corrected for the buoyancy of the air displaced by the increased bulk of the potash after absorbing the gas.

The composition of carbonic oxide was shown by these experiments to be:

Oxygen = **57·16** per cent.
Carbon = **42·84** „

B.—Marsh Gas and Olefiant Gas.

The Burning of Inflammable Gases.

Of the many inflammable gases which had been prepared at different times, hydrogen was the only gas which gave water as the sole product of combustion; and carbonic oxide was the only gas which gave nothing but carbonic anhydride. Other inflammable gases, prepared by heating wood-charcoal or oil, by passing spirit of wine through a red-hot tube, and so forth, gave both water and carbonic anhydride when burnt. They were therefore compounds of carbon and hydrogen, with or without oxygen.

Olefiant Gas or Heavy Carburetted Hydrogen.

The first of these compounds to be prepared in a pure state was OLEFIANT GAS, prepared by the action of sulphuric acid on alcohol. It was examined by a group of Dutch chemists, who showed that it possessed the characteristic property of uniting with chlorine to form an oil, which is still known as DUTCH LIQUID. It was this property which gave rise to the name of "oil-forming" or OLEFIANT GAS. The gas is now called ETHYLENE, and the liquid is called ETHYLENE CHLORIDE.

Composition of Olefiant Gas.

Dalton showed that olefiant gas combined with an equal volume of chlorine to form Dutch liquid:

olefiant gas or ethylene	+	chlorine	=	Dutch liquid or ethylene chloride
1 *vol.*		1 *vol.*		(liquid).

* The solid potash served to prevent the loss of moisture from the absorbing apparatus.

When electric sparks were passed through the gas, it deposited its carbon and left 2 volumes of hydrogen, thus:

olefiant gas	=	carbon	+	hydrogen
1 *vol.*		(solid)		2 *vols.*

When exploded with oxygen it gave water and 2 volumes of carbonic anhydride, whilst 3 volumes of oxygen were used up.

olefiant gas	+	oxygen	=	carbonic anhydride	+	water
1 *vol.*		3 *vols.*		2 *vols.* containing 2 *vols.* of oxygen		(liquid) containing 1 *vol.* of oxygen.

In order to burn the 2 volumes of hydrogen contained in 1 volume of the gas, 1 volume of oxygen would be required; 2 more volumes would be required to produce the 2 volumes of carbonic anhydride; as 3 volumes of oxygen were used in the combustion, there was none present in the gas, which was therefore a HYDROCARBON, that is, a compound containing carbon and hydrogen only.

Marsh Gas or Light Carburetted Hydrogen.

An inflammable gas formed during the decay of vegetable matter, and still commonly known as MARSH GAS, was described by Volta in 1776 in a series of "Letters on the Inflammable Air of Marshes." Volta was able to distinguish it from hydrogen by the fact that it required not $2\frac{1}{2}$ but 10 volumes of air for its combustion.

Dalton showed that its density was 0·6 relatively to air, whilst the density of olefiant gas was 0·9. He therefore called it LIGHT CARBURETTED HYDROGEN.

Composition of Marsh Gas.

Dalton showed that marsh gas could be decomposed by sparking, depositing carbon and yielding (like olefiant gas) 2 volumes of hydrogen.

marsh gas	=	carbon	+	hydrogen
1 *vol.*		(solid)		2 *vols.*

When exploded with oxygen, of which 2 volumes are used, water is produced, but only 1 volume of carbonic anhydride.

marsh gas	+	oxygen	=	carbonic anhydride	+	water
1 *vol.*		2 *vols.*		1 *vol.* containing 1 *vol.* of oxygen		(liquid) containing 1 *vol.* of oxygen.

Like olefiant gas, marsh gas was shown to be a hydrocarbon, since the whole of the 2 volumes of oxygen required to burn 2 volumes of hydrogen and to produce 1 volume of carbonic anhydride had to be supplied in the free state during the combustion. It will be noticed that olefiant gas and marsh gas both contain 2 volumes of hydrogen in

1 volume of the gas; but they differ in that olefiant gas gives 2 volumes instead of 1 volume of carbonic anhydride; it therefore contains twice as much carbon as an equal volume of marsh gas.

C.—THE COMBUSTION OF ORGANIC COMPOUNDS.

Early Organic Analyses.

As soon as it was known that organic substances were compounds containing carbon and hydrogen, experiments were made to determine the proportions of these two elements. Thus, Lavoisier in 1784 burnt spirit of wine over mercury in a bell-jar filled with air, to which measured volumes of oxygen were supplied from a second bell-jar inverted over

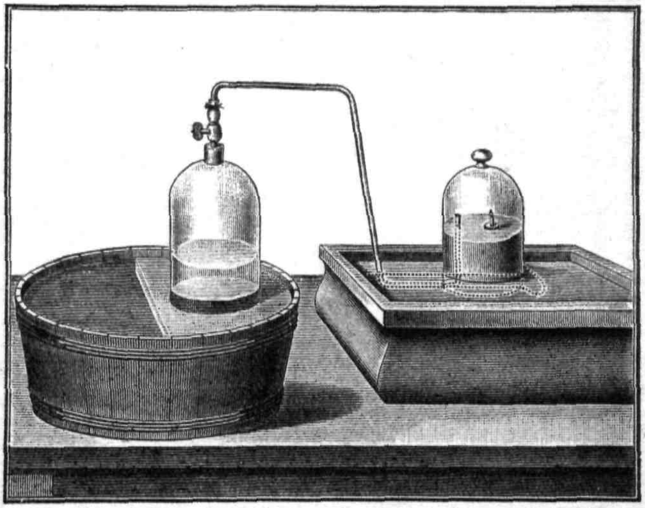


FIG. 53.—LAVOISIER'S APPARATUS FOR BURNING SPIRIT OF WINE IN AIR OR OXYGEN.

water (Fig. 53). The quantity of *carbon* in the spirit of wine was calculated from the volume of carbonic anhydride produced; the weight of water (calculated by subtracting the weight of carbonic anhydride from that of spirit of wine and oxygen) gave the weight of *hydrogen*.

The determination of carbon and hydrogen in olive oil and in the wax of a candle was carried out in a similar manner; but none of these analyses gave figures which would now be recognised as correct. More exact results were obtained (by Gay-Lussac and Thenard in 1810, and by Berzelius in 1815) when the organic compounds were burnt with the help of oxygen supplied in the form of potassium chlorate; but a final solution of the problem of organic combustion was only achieved when copper oxide came to be used as the main source of oxygen

Combustion with the Help of Copper Oxide.

Copper oxide was used by Gay-Lussac in 1815 for the combustion of cyanogen gas, and by Berzelius and Dulong in 1820 for the combustion of hydrogen (p. 88); but it was first used systematically for organic analysis by Liebig (1831), who also introduced the well-known Liebig "potash bulbs" for absorbing and weighing carbonic anhydride.*

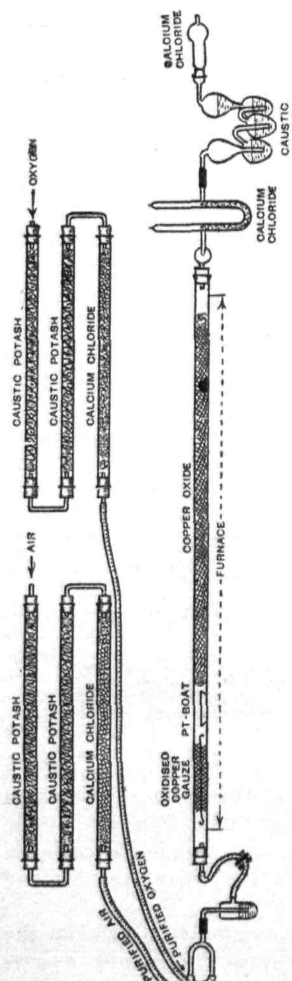


FIG. 54.—APPARATUS FOR COMBUSTION OF ORGANIC COMPOUNDS.

Modern apparatus for the combustion of organic compounds is shown in Fig. 54. It consists essentially of three parts:—

(*a*) A *purifying apparatus*, in which air and oxygen are freed from carbonic anhydride and moisture.

(*b*) A *combustion apparatus*, in which the organic compound is burnt with the help of air, oxygen, and copper oxide (or some similar oxidising agent such as lead chromate).

(*c*) An *absorption apparatus*, for collecting and weighing the moisture and carbonic anhydride produced in the combustion.

As the quantity of substance burnt is small (about 0·2 gram) it is very important that the apparatus should be entirely free from all traces of moisture and carbonic anhydride other than those produced by the combustion. Carbonic anhydride is removed by heating the combustion tube, and passing through it air which has been purified with the help of soda-lime (*i.e.*, quicklime which has been slaked with a strong solution of caustic soda and graded into particles of uniform size) or solid potash. Much greater difficulty is experienced in removing moisture, since a single milligram of water may impair the accuracy of the analysis. In addition to tubes charged with soda-lime or potash, the purifying apparatus therefore contains

* The original form of Liebig's potash bulbs is shown at 10 and 11 in Fig. 44, p. 79.

a column of calcium chloride; but prolonged heating of the combustion-tube is required before the whole of the moisture is driven out of the apparatus in readiness for the combustion. A tiny wash-bottle containing concentrated sulphuric acid serves to show the rate at which purified air or oxygen is passed into the combustion-tube.

The water produced by the combustion is absorbed in a U-tube containing calcium chloride, or pumice wetted with concentrated sulphuric acid. When Liebig's potash bulbs are used to absorb the carbonic anhydride, great care is required to ensure that gas does not pass through them at any time at a greater rate than about three bubbles per second. Even when the current of gas is slow, the bubbles pass so quickly through the aqueous potash that there is no time for carbonic anhydride to be absorbed except from the surface of each bubble; most of the absorption therefore takes place in the wet tubes connecting the bulbs. Much better absorption is obtained in the apparatus shown in Fig. 55. The substance to be burnt is weighed out into a narrow "boat" of platinum or porcelain and is stored in a desiccator to keep it dry. It is inserted between a long column of copper oxide (made by burning copper wire), which is kept hot after the preliminary heating of the combustion-tube, and a roll of oxidised copper gauze, which is allowed to cool before it is withdrawn to insert the boat into the tube. The burners under the gauze are then lighted and the heat is allowed very cautiously to spread to the boat, which is, however, finally heated to redness. The combustion is usually begun in a current of air and continued in oxygen; but finally, when the combustion has been finished, dry air must be passed through the apparatus in order to displace the oxygen from the absorption vessels. Modifications of this process are used when the substance to be burnt contains other elements in addition to carbon, hydrogen, and oxygen.

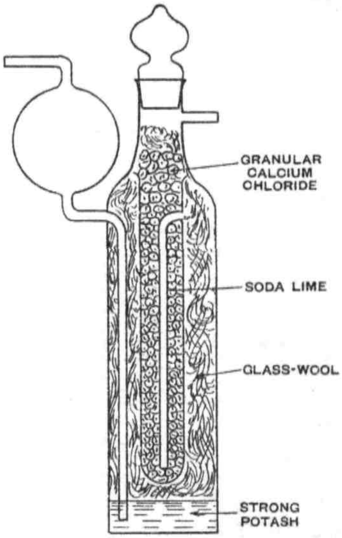


FIG. 55.—APPARATUS FOR ABSORPTION OF CARBONIC ANHYDRIDE.

The gas passes in through a safety-bulb, sufficiently large to hold the whole of the liquid absorbent, in case this should be drawn back by the rapid absorption of gas. It bubbles through a short column of strong potash, but is "scrubbed" much more effectively by glass-wool which has been wetted with the potash by tilting the tube. From the top of the column of glass-wool, it passes to the bottom of a column of solid absorbent, consisting of granular soda-lime, covered with a little granular calcium chloride to complete the drying of the gas.

The method of working out the results of a combustion is shown in the following example :—

0·2317 gram of alcohol gave on combustion 0·2731 gram of water and 0·4415 gram of carbonic anhydride.

Since water contains one-ninth of its weight of hydrogen, and

carbonic anhydride contains three-elevenths of its weight of carbon, the weights of hydrogen and of carbon in the alcohol are :

$$\text{Hydrogen} = \frac{0{\cdot}2731}{9} = 0{\cdot}03034 \text{ gram}$$

$$\text{Carbon} = \frac{0{\cdot}4415 \times 3}{11} = 0{\cdot}12041 \text{ gram};$$

the remainder of the substance, 0·08095 gram, is assumed to be oxygen.

The percentage composition of alcohol according to this experiment is therefore :—

$$\text{Carbon} = \frac{0{\cdot}12041 \times 100}{0{\cdot}2317} = 52{\cdot}0 \text{ per cent.}$$

$$\text{Hydrogen} = \frac{0{\cdot}03034 \times 100}{0{\cdot}2317} = 13{\cdot}1 \quad ,,$$

$$\text{Oxygen} = \frac{0{\cdot}08095 \times 100}{0{\cdot}2317} = 34{\cdot}9 \quad ,,$$

SUMMARY AND SUPPLEMENT.

1. **Lassone,** in 1776, prepared an inflammable oxide of carbon by heating Prussian blue, and by heating zinc oxide with charcoal,

$$ZnO + C = Zn + CO.$$

It differed from hydrogen in that it burned with a beautiful blue flame, and could not be detonated when mixed with air or oxygen. The same gas was prepared by **Priestley** in 1783 by heating smithy scale with charcoal,

$$Fe_3O_4 + 4C = 3Fe + 4CO.$$

2. **Cruikshank,** in 1801, prepared the gas, free from hydrogen, by heating carbonated baryta (barium carbonate) or chalk (calcium carbonate) with iron plates,

$$4BaCO_3 + 3Fe = 4BaO + 4CO + Fe_3O_4,$$
$$4CaCO_3 + 3Fe = 4CaO + 4CO + Fe_3O_4.$$

He showed that when exploded with oxygen in Volta's eudiometer (pp. 253 and 368) it combined with half its volume of oxygen and gave an equal volume of carbonic anhydride ; he therefore regarded it as a lower oxide of carbon and called it "gaseous oxide of carbon," now **carbonic oxide,**

$$\underset{\substack{\text{Carbonic oxide} \\ 1\ vol.}}{2CO} + \underset{\substack{\text{Oxygen} \\ \frac{1}{2}\ vol.}}{O_2} = \underset{\substack{\text{Carbonic anhydride.} \\ 1\ vol.}}{2CO_2}$$

3. **Désormes and Clément,** in 1801, proved by similar experiments that Lassone's inflammable gas was an oxide of carbon which gave an equal volume of carbonic anhydride but no water when burnt. They prepared it by the action of charcoal on carbonated baryta,

$$BaCO_3 + C = BaO + 2CO,$$

a refractory carbonate which could not be decomposed by heat alone. They

could not prepare it by direct combustion of charcoal in air or oxygen, but found that fixed air could be reduced to carbonic oxide by red-hot charcoal,

$$CO_2 + C = 2CO.$$

They also prepared a mixture of carbonic oxide and hydrogen by the action of red-hot charcoal on steam,

$$H_2O + C = H_2 + CO.$$

4. **Stas,** in 1849, determined the gravimetric composition of carbonic oxide by passing the gas over weighed copper oxide and weighing the carbonic anhydride produced,

$$CO + CuO = Cu + CO_2.$$

5. **Volta,** in 1776, distinguished *marsh gas*, or *methane*, CH_4, from hydrogen by the fact that it required about 10 times (instead of $2\frac{1}{2}$ times) its volume of air for combustion. Another inflammable hydrocarbon, *olefiant gas*, or *ethylene*, C_2H_4, prepared by the action of oil of vitriol on alcohol,

$$\underset{\text{Alcohol}}{C_2H_6O} = \underset{\text{Ethylene}}{C_2H_4} + \underset{\text{Water}}{H_2O},$$

was called olefiant gas by a group of Dutch chemists because it combined with chlorine to form an oily liquid.

$$\underset{\text{Ethylene}}{C_2H_4} + \underset{\text{Chlorine}}{Cl_2} = \underset{\text{Ethylene chloride}}{C_2H_4Cl_2}.$$

6. **Dalton,** in 1810, determined the volumetric composition of these gases as follows :—

By sparking, carbon was deposited, and hydrogen (2 vols.) was set free.

$$\underset{1\ vol.}{CH_4} = C + \underset{2\ vols.}{2H_2}$$

$$\underset{1\ vol.}{C_2H_4} = 2C + \underset{2\ vols.}{2H_2}$$

By explosion with excess of oxygen

$$\underset{\substack{\text{Marsh gas}\\ 1\ vol.}}{CH_4} + \underset{\substack{\text{Oxygen}\\ 2\ vols.}}{2O_2} = \underset{\substack{\text{Carbonic anhydride}\\ 1\ vol.}}{CO_2} + \underset{\text{Water (liquid)}}{2H_2O} \quad \therefore \text{Contraction} = 2\ vols.$$

$$\underset{\substack{\text{Ethylene}\\ 1\ vol.}}{C_2H_4} + \underset{\substack{\text{Oxygen}\\ 3\ vols.}}{3O_2} = \underset{\substack{\text{Carbonic anhydride}\\ 2\ vols.}}{2CO_2} + \underset{\text{Water (liquid)}}{2H_2O} \quad \therefore \text{Contraction} = 2\ vols.$$

When exploded with less oxygen.

$$\underset{\substack{\text{Marsh gas}\\ 1\ vol.}}{CH_4} + \underset{\substack{\text{Oxygen}\\ 1\ vol.}}{O_2} = \underset{\substack{\text{Carbonic oxide}\\ 1\ vol.}}{CO} + \underset{\substack{\text{Hydrogen}\\ 1\ vol.}}{H_2} + \underset{\text{Water}}{H_2O} \quad \therefore \text{No contraction.}$$

$$\underset{\substack{\text{Olefiant gas}\\ 1\ vol.}}{C_2H_4} + \underset{\substack{\text{Oxygen}\\ 1\ vol.}}{O_2} = \underset{\substack{\text{Carbonic oxide}\\ 2\ vols.}}{2CO} + \underset{\substack{\text{Hydrogen}\\ 2\ vols.}}{2H_2} \quad \therefore \text{Expansion} = 2\ vols.$$

7. The combustion of organic compounds is carried out by oxidation with copper oxide : the water collected gives the proportion of hydrogen, and the carbon dioxide gives the proportion of carbon in the compound.

CHAPTER X

THE LAWS OF CHEMICAL COMBINATION

The Study of Chemical Combination.

In the preceding chapters, a description has been given of the methods by which substances may be purified, and the characteristics of the pure substances determined. Illustrations have also been given of the way in which the composition of chemical compounds may be determined :—

(i) By ANALYSIS, as in the burning of chalk to lime.
(ii) By SYNTHESIS, as in the burning of copper to copper oxide, hydrogen to water, or carbon to carbonic anhydride.
(iii) By more complex methods of "analysis" as in the combustion of alcohol.

The exact study of chemical composition, which began with Black's work in 1755, was continued by Lavoisier and then engaged the attention of many workers in every country. These early analyses soon showed that chemical combination could not be brought about in an arbitrary manner according to the whim of the worker, but was controlled by natural laws .

These laws of chemical combination are now known as :—

(i) The Law of Fixed Proportions.
(ii) The Law of Multiple Proportions.
(iii) The Law of Reciprocal Proportions.

These three laws can be interpreted and explained very readily by means of Dalton's Atomic Theory (Chapter XI).

The Law of Fixed Proportions.

The work of Black and of Lavoisier was based upon the tacit assumption that—

"*Chemical compounds are formed by the combination of their elements in fixed proportions by weight.*"

Apart from this LAW OF FIXED PROPORTIONS, it would have been of little use to place on record, as one of the constants of Nature, the proportion of lime which can be obtained from chalk ; or, conversely,

the quantity of chalk that can be prepared from a given quantity of lime.

The first definite statement of the law was, however, made by Proust in 1799, when he found that native carbonate of copper had the same composition as the carbonate prepared artificially in the laboratory. He concluded that the formation of compounds was controlled by an invisible hand, which fixed both their composition and their attributes. In a similar way, Proust showed that, " in art as in Nature," copper was never oxidised beyond 26 per cent. ; this proportion was fixed by Nature, and the power of augmenting or diminishing it was not given to man.

Fixed Proportions as a Test of Chemical Combination.

The law of fixed proportions was challenged in 1803 by Berthollet, who maintained that the elements could combine in variable proportions, and that constant composition was only secured when some component crystallised out or distilled out from the interacting mixture. Proust, who undertook a detailed criticism of the different cases quoted by Berthollet, was able to appeal to the general feeling of chemical workers in support of the view that there are, in fact, two different kinds of combination. Thus, no formal proof was needed to show that the dissolving of sugar in water was quite a different process from the union of carbon, hydrogen, and oxygen, whereby the sugar itself was produced. Again, the dissolution of saltpetre in water was evidently of a different character from the combination of nitric acid and potash to produce saltpetre. Proust showed that in the former case the proportions of sugar and water or of saltpetre and water might be varied within wide limits, whilst the combination of carbon, hydrogen, and oxygen, or of nitric acid and potash, could only take place under the rigid condition of a fixed proportionality between the constituents. He therefore proposed to use this difference as a means of distinguishing between solutions and chemical compounds. Thus, the composition of a SOLUTION or MIXTURE may vary, but a definite COMBINATION or CHEMICAL COMPOUND must obey the LAW OF FIXED PROPORTIONS and will not be recognised as such if it fails to conform with this law.

The Law of Multiple Proportions.

The LAW OF MULTIPLE PROPORTIONS, which was discovered by Dalton about 1808 and tested by Berzelius in 1810, states that—

> " *If several compounds be formed, the fixed proportions in which two elements combine together are in simple integral ratios to one another.*"

In several cases elements can unite together in different proportions. Proust recognised this fact, and asserted that there was a definite maximum proportion and a definite minimum proportion, which represented

distinct chemical compounds, and that all products of intermediate composition were mixtures. Thus, in the case of iron and sulphur, he found a minimum proportion of sulphur in the artificial sulphide :

$$\textit{iron} : \textit{sulphur} = 100 : 60$$

and a maximum proportion in iron pyrites :

$$\textit{iron} : \textit{sulphur} = 100 : 90.$$

These two fixed proportions are in the simple ratio

$$60 : 90 = 2 : 3 ;$$

but, as the correct proportions are

$$57 : 114 = 1 : 2,$$

it is not surprising that Proust was unable to detect any simple relationship in his equally rough analyses of other compounds.

Dalton, on the other hand, was led by his atomic theory to recognise that the different fixed proportions must be in simple ratios to one another. He therefore set out the composition of the two oxides of carbon in such a way as to show that carbon united with just twice as much oxygen in forming carbonic anhydride as in forming carbonic oxide, whilst the proportion of carbon to hydrogen in olefiant gas was just twice as great as the proportion of carbon to hydrogen in marsh gas. He also set out the composition of three oxides of nitrogen, in which the elements were united in the ratios

$$\textit{oxygen} : \textit{nitrogen} = 10 : 7$$
$$\textit{oxygen} : \textit{nitrogen} = 5 : 7$$
$$\textit{oxygen} : \textit{nitrogen} = 5 : 14$$

these proportions being in the ratio of 4 : 2 : 1.

In this case there is a definite compound of intermediate composition in addition to Proust's maximum and minimum. Other examples of multiple proportions amongst gases were quoted by Gay-Lussac in 1809 when he put forward his "Law of Volumes" (p. 124).

Multiple Proportions in the Formation of Salts.

(*a*) *Carbonates and Bicarbonates.*—The discovery of BICARBONATES was made by Black in 1755. He exposed a solution of potassium carbonate to the air in a shallow vessel for a space of two months and found that the solution deposited crystals, which were milder than the ordinary carbonate, and bore a much closer resemblance to neutral salts. Black showed that the crystalline product had been formed by the absorption of fixed air from the atmosphere, and that this gas was liberated with violent effervescence as soon as the least trace of acid was added to the salt. Cavendish in 1766 showed that the quantity of acid which liberated 100 parts of fixed air from marble set free 109 parts from ordinary potassium carbonate and 211 parts from Black's salt. The latter compound therefore contained twice as much fixed air,

relatively to its neutralising power, as the former. It is for this reason that the salt is generally described as POTASSIUM BICARBONATE. Cavendish's analysis was confirmed in 1808 by Wollaston, who showed that 4 grains of bicarbonate, when converted by heat into carbonate, lost the same amount of fixed air as 2 grains of the same salt when wholly decomposed by acids.

(*b*) *Sulphates and Bisulphates.*—Wollaston showed that a similar relationship existed between the SULPHATE formed by neutralising potash with sulphuric acid and the BISULPHATE which is formed by adding twice as much acid as is necessary for neutralisation.

(*c*) *Oxalates, Binoxalates, and Quadroxalates.*—It was already known that two series of oxalates existed, namely, the NEUTRAL OXALATES and the BINOXALATES, the latter containing twice as much acid as was necessary to neutralise the base. Wollaston showed that a crystalline QUADROXALATE could be prepared by using four times as much acid as was required for neutralisation. In these three oxalates equal quantities of alkali are united with 1 : 2 : 4 parts of acid, these ratios being identical with those discovered by Dalton in the three oxides of nitrogen.

Berzelius (1810) states and proves the Law of Multiple Proportions.

The Swedish chemist Berzelius was one of the first to undertake an exact study of the laws of chemical combination. He made many improvements in analytical methods, and attained to a much higher degree of accuracy than Proust had reached. Berzelius made the first formal statement of the law of multiple proportions and proved its correctness in five cases as follows :—

	Lead and Oxygen.	
Brown oxide . .	100 : 15·6	Ratio 2·00 : 1
Yellow oxide . .	100 : 7·8	
	Sulphur and Oxygen.	
*Sulphuric acid** .	100 : 146·427	Ratio 1·497 : 1
*Sulphurous acid** .	100 : 97·83	
	Copper and Oxygen.	
Black oxide . .	100 : 25	Ratio 2·00 : 1
Red oxide . .	100 : 12·5	
	Iron and Sulphur.	
Maximum . .	100 : 117	Ratio 1·993 : 1
Minimum . .	100 : 58·73	
	Iron and Oxygen.	
Ferric oxide . .	100 : 44·25	Ratio 1·495 : 1
Ferrous oxide . .	100 : 29·6	

* *i.e.*, Sulphuric anhydride and sulphurous anhydride.

Berzelius recognised cases in which substances combined together in the ratio $a:b$, $2a:3b$, $a:2b$, and $a:4b$, but did not find any case in which the ratio was $a:3b$.

Accuracy of the Law of Multiple Proportions.

Stas's analysis of the two oxides of carbon may be used as evidence that the Law of Multiple Proportions (unlike Gay-Lussac's law of volumes, see p. 125) is exact and not merely approximate. Dumas and Stas found in 1841 that 100 parts of carbonic anhydride contain :

Carbon . . . 27·27 per cent.
Oxygen . . . 72·73 per cent.

Stas in 1849 showed that 100 parts of carbonic anhydride are formed from :—

Carbonic oxide . . 63·64 per cent.
Oxygen . . . 36·36 per cent.

It follows that 27·27 grams of carbon unite with $63{\cdot}64 - 27{\cdot}27 = 36{\cdot}37$ grams of oxygen to form 63·64 grams of carbonic oxide ; and with 72·73 grams of oxygen to form 100 grams of carbonic anhydride. The ratio $\frac{72{\cdot}73}{36{\cdot}37} = 1{\cdot}9997$ differs by only one part in 7000 from the exact ratio 2 : 1.

The Law of Reciprocal Proportions.

The LAW OF RECIPROCAL PROPORTIONS states that—

> "*The relative proportions in which two elements combine with a third element are in a simple ratio to those in which they combine* (a) *with one another or* (b) *with a fourth element.*"

(*a*) In water, hydrogen and oxygen are combined in the proportion

1 *part of hydrogen* : 8 *parts of oxygen.*

In marsh gas, hydrogen and carbon are combined in the proportion

1 *part of hydrogen* : 3 *parts of carbon,*

whilst in olefiant gas the proportion is

1 *part of hydrogen* : 6 *parts of carbon.*

What will happen if oxygen, on the one hand, combines with carbon on the other ? The Law of Reciprocal Proportions suggests that the elements will combine in the proportion of

8 *parts of oxygen* : 3 *parts of carbon* or
8 *parts of oxygen* : 6 *parts of carbon.*

Actually, 3 oxides of carbon are known in which the proportions are as follows :—

Carbonic anhydride, *oxygen* : *carbon* = 8 : 3
Carbonic oxide, *oxygen* : *carbon* = 8 : 6
Carbon suboxide, *oxygen* : *carbon* = 8 : 9

(*b*) Suppose that oxygen and carbon unite with a fourth element such as sulphur. The Law of Reciprocal Proportions suggests that 3 *parts of carbon* and 8 *parts of oxygen*, which have been shown to unite with equal weights of hydrogen, will also unite with equal weights of sulphur; or that some simple multiples of these numbers will be involved. In practice it is found that 16 *parts of sulphur* unite with 3 *parts of carbon* and with 16 *or* 24 *parts of oxygen.*

The Law of Reciprocal Proportions and the Theory of Equivalents or Combining-weights.

The law of reciprocal proportions leads directly to the idea that each element has a definite COMBINING-WEIGHT or EQUIVALENT, and that when elements combine together they do so in simple multiples of these quantities. Thus, in the examples already quoted, it is clear that *one part of hydrogen, three parts of carbon, eight parts of oxygen,* and *sixteen parts of sulphur* represent in the simplest possible way the relative weights of these elements which are found in combination with each other or with other elements. The importance of these equivalents or combining-weights consists in the fact that when they have once been determined by means of a small number of very careful analyses, they can be used to calculate the exact composition of all the other compounds of these elements. This fact was realised for the first time in 1807 by Berzelius, who devoted most of his life to the accurate analyses that are needed to establish a correct table of equivalents. Even greater care and painstaking accuracy were shown in the measurements of Stas extending over more than forty years, from 1840 to 1882. In recent years much work of this character has been carried out at Harvard University by Professor T. W. Richards.

Definition of Equivalents or Combining-weights.

In establishing a table of equivalents or combining-weights it is necessary to select the fixed weight of some one element as a standard. Dalton in 1808 selected one part of hydrogen. This standard has been used very widely, in accordance with the following definition:

> "*The equivalent weight of an element is that weight which combines with or takes the place of one part by weight of hydrogen.*"

In this definition the smallest of the equivalents is selected as the standard, so that all the others are greater than unity. In practice, however, the analyses commonly used in determining equivalents are those of oxides rather than of hydrides. Even when an element combines with hydrogen it is not easy to obtain accurate analyses of the hydride except by burning both constituents to oxides. In the case of metals, very few hydrides are known and the determination of the equivalent

relatively to hydrogen involves the measurement of two ratios, *e.g.*, taking the ratios out to half a unit only, we have

$$\begin{cases} copper : oxygen = 100 : 25{\cdot}5 \\ hydrogen : oxygen = 1 : 8 \end{cases}$$

$$\text{whence} \qquad copper : hydrogen = \frac{100}{25{\cdot}5} \div \frac{1}{8} = 31{\cdot}5 : 1.$$

In practice, the ratio *metal* : *oxygen* can usually be determined with greater ease and accuracy than the ratio *hydrogen* : *oxygen*; but this additional accuracy is lost when the two ratios are combined to give the ratio *metal* : *hydrogen*, which is the hydrogen-equivalent of the metal.

For this reason many workers have preferred to express the equivalents relatively to a fixed weight of oxygen. Thus, Stas used 1000 parts of oxygen and Dulong and Petit used 1 part of oxygen as the standard. At the present time, 8 parts of oxygen are used as the standard, and the equivalent of an element may be defined as follows :—

"*The equivalent of an element is that weight of the element which combines with or takes the place of* 8 *parts by weight of oxygen.*"

These equivalents differ but little from those which are obtained when hydrogen equals 1, since in the new scheme the equivalent of hydrogen is changed only to 1·0075. They have the advantage that they depend directly on the results of a single analysis, and do not involve a knowledge of the composition of water. It also happens that many of the equivalents approach much more nearly to whole numbers when oxygen equals 8 exactly and hydrogen equals 1·0075, than when hydrogen is taken as exactly 1 and oxygen equals 7·9394.

TABLE 7.—EQUIVALENTS OF ELEMENTS.

Non-metals.		*Metals.*	
Hydrogen	1·0075	Calcium	20·03
Carbon	3·001	Sodium	23·00
Oxygen exactly	**8**	Copper	31·78
Nitrogen (in nitrous oxide)	14·008	Potassium	39·10
		Mercury	100·3
Sulphur	16·03	Lead	103·60
Chlorine	35·46	Silver	107·88

The table shows at a glance the composition of lime as containing 20·03 parts of calcium combined with 8 parts of oxygen, whilst litharge contains 103·60 parts of lead combined with 8 parts of oxygen. Muriate of lime or calcium chloride contains 20·03 parts of calcium combined with 35·46 parts of chlorine, whilst common salt contains 23·00 parts of sodium combined with 35·46 parts of chlorine.

In drawing up a table of equivalents it is customary, when multiple

proportions are observed, to tabulate the equivalent of the element as deduced from the analysis of one compound, selected as typical, and to represent the composition of the others by multiples of the tabulated equivalents. Thus, in the table, carbon and oxygen are shown as uniting together in the ratio 3·00 to 8 to form carbonic anhydride: but they also unite in the ratio 2 × 3·00 to 8 to form carbonic oxide. Again, carbon and hydrogen unite in the ratio 3·00 to 1·0075 in marsh gas, but in the ratio 2 × 3·00 to 1·0075 in olefiant gas.

Reciprocal Proportions in the Neutralisation of Acids and Alkalies.

Like many other important discoveries in chemistry, the doctrine of equivalents or combining-weights originated in the study of the formation of salts by the neutralisation of acids and alkalies. As long ago as 1767 those weights of potash and of marble which would neutralise the same quantity of acid had been described by Cavendish as EQUIVALENT to one another; and in 1788 he had tacitly assumed the law of reciprocal proportions when he recognised that quantities of nitric and sulphuric acids which neutralised equal weights of potash would also decompose equal weights of marble. On these lines it was possible to construct a table of equivalents which may be set out as follows:—

TABLE 8.—EQUIVALENT QUANTITIES OF BASES AND ACIDS

Caustic potash	112	will neutralise and be neutralised by	Nitric acid	126
MARBLE	100		Acetic acid	120
Caustic soda	80		Sulphuric acid	98
Lime	56		Muriatic acid	73
Ammonia	34			

A table of this kind, in which 1000 parts of sulphuric acid was selected as the standard, was published in 1802, some years before Dalton's Atomic Theory had led Berzelius to formulate definitely the law of reciprocal proportions.

The Equivalents of Compounds.

The examples quoted in the preceding paragraph show that it is possible to draw up a table of equivalents, not only for elements, but also for compounds.

(*a*) *Oxides, Hydrides, Chlorides, etc.*—In the case of simple oxides, hydrides, chlorides, etc., the equivalent may be defined as that weight of the compound which contains 8 *parts of oxygen* or 1·0075 *parts of hydrogen*, or 35·46 *parts of chlorine*. In the case of metallic compounds, the weight of the compound which contains *one equivalent of metal* is usually taken as the equivalent.

(*b*) *Acids and Bases.*—Acids are now usually regarded as compounds (with a sour taste, etc.) from which, in the act of neutralisation,

hydrogen may be displaced by metals. This leads to the following definitions :—

> "*The equivalent of an acid is that weight of the acid which contains* 1·0075 *parts of hydrogen displaceable by a metal.*"
>
> "*The equivalent of an alkali or base is the quantity that is required to neutralise one equivalent of an acid.*"

In the case of metallic bases * we may give an alternative definition :—

> "*The equivalent of an alkali or of a metallic base is that quantity which contains enough metal to displace* 1·0075 *grams of hydrogen from an acid.*"

The equivalents of acids and bases as thus defined are just half of those shown in the table above, since it happens that the equivalent weight of marble is almost exactly 50. Thus, 50 parts of marble yield when burnt 28 parts of lime, containing 20 parts of metallic calcium (one equivalent) united with 8 parts (or one equivalent) of oxygen.

(*c*) *Oxidising and Reducing Agents.*—The equivalent of an OXIDISING AGENT is that weight which contains 8 parts of oxygen available for oxidation, and which will oxidise 1·0075 parts of hydrogen. In the same way, the equivalent of a REDUCING AGENT is the quantity that will remove 8 parts of oxygen or provide 1·0075 parts of hydrogen.

SUMMARY AND SUPPLEMENT.

1. **The Law of Fixed Proportions** states that

> "*Chemical compounds are formed by the combination of their elements in fixed proportions by weight.*"

2. **The Law of Multiple Proportions** states that

> "*If several compounds be formed, the fixed proportions in which two elements combine together are in simple integral ratios to one another,*"

e.g., *iron* and *sulphur* combine in the ratios 100 : 57 or 100 : 114, *nitrogen* and *oxygen* combine in the ratios 14 : 8, 14 : 16, 14 : 32.

3. **The Law of Reciprocal Proportions** states that

> "*The relative proportions in which two elements combine with a third element are in a simple ratio to those in which they combine* (a) *with one another or* (b) *with a fourth element.*"

Thus, starting with		*hydrogen* : *oxygen*	=	1 : 8
and		*hydrogen* : *carbon*	=	1 : 3 or 1 : 6 ;
we find	(*a*)	*oxygen* : *carbon*	=	8 : 3 or 8 : 6 or 8 : 9
and	(*b*)	*sulphur* : *oxygen*	=	16 : 2 × 8 or 16 : 3 × 8
		sulphur : *carbon*	=	16 : 3.

4. The **Combining-weight** or **Equivalent** of an element is the weight which will combine with or replace 8 *parts of oxygen*, or (as secondary standards) 1·0075 *parts of hydrogen* or 35·46 *parts of chlorine*.

* Some basic compounds, such as ammonia, do not contain a metal.

5. The **equivalent of an acid** is the weight which contains 1·0075 parts of hydrogen replaceable by a metal in neutralisation :

e.g., 49 parts of sulphuric acid, H_2SO_4
63 parts of nitric acid, HNO_3
36·5 parts of hydrochloric acid, HCl.

The **equivalent of an alkali** or a base is the weight which will neutralise one equivalent of acid :

e.g., 40 parts of caustic soda, NaOH
53 parts of sodium carbonate, Na_2CO_3
50 parts of chalk, $CaCO_3$.

A solution containing one gram-equivalent of an acid or a base in a litre, *e.g.*, 49 grams of sulphuric acid or 40 parts of caustic soda, is called a **normal solution;** a solution containing one-tenth of this quantity, *e.g.*, 4·9 grams of H_2SO_4, or 4·0 grams of NaOH, is called a **decinormal solution.** A normal solution of an oxidising agent would contain 8 grams of available oxygen in a litre, and a litre of a decinormal solution would contain 0·8 gram.

CHAPTER XI

THE ATOMIC THEORY

The Theory of Atoms.

From the time of the Greek philosophers, the theory had been held that the subdivision of matter must ultimately reach a limit beyond which the particles could not be divided further. These indivisible particles were called ATOMS (Greek ἀ, not; τέμνω, I cut). The detailed study of the properties of matter which took place from the time of Boyle onwards confirmed the idea that all forms of matter are made up of these tiny particles, which Newton described as " solid, massy, hard, impenetrbale, movable and indestructible."

Dalton's Atomic Theory.

This vague theory of atoms was of little value until Dalton, about 1802, added to it certain novel features, and showed that it could then be used to explain the laws of chemical combination. Dalton suggested that—

(i) The ultimate particles of a pure substance, whether simple or compound, are perfectly alike in size and weight.

(ii) The " simple atoms " of an elementary substance are indivisible, and can neither be created nor destroyed.

(iii) The " compound atoms " (or " molecules "; see below) of a compound are formed by the union of two or more elementary atoms.

(iv) Combination between atoms takes place in the simplest integral ratios, *e.g.*, 1 atom of *A* with 1, 2, or 3 atoms of *B*.

The groups of " simple atoms," which Dalton called " compound atoms," cannot be separated without destroying the compound ; but as they are not indivisible, they are now generally described as MOLECULES (*i.e.*, little masses, Latin, *moles*, a mass) rather than atoms.

Recent work has made necessary some further modifications of Dalton's atomic theory, thus :—

(i) Many substances which have been regarded until recently as pure, simple substances, or elements (*e.g.*, chlorine), have been proved to be mixtures of two or more " isotopic " elements (p. 540), resembling one another so closely that it is very difficult indeed to separate them ; their compounds are also

mixtures of compounds of each of the various "isotopes." Each constituent of a group of isotopic elements is, however, composed of atoms of which the mass is uniform within extremely narrow limits. Although, therefore, many of the traditional elements must now be classed as mixtures, the direct comparison of the masses of the atoms has provided a very remarkable verification of Dalton's first postulate.

(ii) The atoms of a "radioactive element" (p. 539) are continually undergoing spontaneous destruction or disintegration into atoms of smaller atomic weight; this cannot be accelerated or retarded by any method that has yet been tried, but in the case of nitrogen it is believed that the destruction of the atom, involving its disintegration into atoms of smaller atomic weight, has been brought about by artificial methods. Although the atom is therefore no longer indivisible, the name has been retained to represent the particles of the element which pass unchanged through all the ordinary operations of the chemical laboratory.

Atomic Symbols.

Dalton represented the atoms by means of symbols, *e.g.*, hydrogen ⊙, oxygen ○, water ⊙○. This pictorial representation had much to do with the success of Dalton's theory. It was improved by Berzelius, who suggested, in 1819, that the elements might be represented more conveniently by their initial letters, *e.g.*, Hydrogen H, Oxygen O, Water HO.

When several elements had the same initial letter, Berzelius proposed to use a single letter to represent the chief non-metallic element and to add a second letter to distinguish the metals, or other nonmetals having the same initial. As examples he gives: –

S	= Sulphur	C	= Carbonicum (carbon)
Si	= Silicium (silicon)	Co	= Cobaltum (cobalt)
Sb	= Stibium (antimony)	Cu	= Cuprum (copper)
Sn	= Stannum (tin)		

The majority of Berzelius's symbols are easily recognised abbreviations; exceptions are found in the case of elements which are represented by entirely different names in Latin and in English, *e.g.*,

Gold	Aurum	Au
Silver	Argentum	Ag
Copper	Cuprum	Cu
Iron	Ferrum	Fe
Lead	Plumbum	Pb
Tin	Stannum	Sn
Mercury	Hydrargyrum*	Hg
Antimony	Stibium	Sb
Sodium	Natrium	Na
Potassium	Kalium	K

* From Greek ὕδωρ, water; ἄργυρος, silver; *i.e.*, liquid silver or "quicksilver."

The Laws of Chemical Combination explained by the Atomic Theory.

The chief merit of Dalton's atomic theory was the simple and obvious explanation which it gave of the laws of chemical combination.

(*a*) *The Law of Fixed Proportions.*—The fixed proportions of hydrogen and oxygen in water followed at once from Dalton's assumption that all the atoms of hydrogen and all those of oxygen were exactly alike in size and weight. Different proportions could only arise if the atoms were combined in different ratios, giving rise to totally different compounds.

(*b*) *The Law of Multiple Proportions.*—The law of multiple proportions was actually discovered by Dalton as a consequence of his enunciation of the atomic theory. Proust, studying the facts alone, did not recognise this law, and Dalton's analyses could scarcely have led him to it if he had not been guided by theory. But assuming the atomic theory to be correct, it was evident that if two elements, *A* and *B*, were disposed to combine, they must do so in ratios such as—

one atom of *A* : one atom of *B*
one atom of *A* : two atoms of *B*
two atoms of *A* : one atom of *B*, etc.

Combinations of this kind would obviously conform to the law of multiple proportions as set out in the preceding chapter.

(*c*) *The Law of Reciprocal Proportions.*—The law of reciprocal proportions may be summed up in the statement that *each element has its own characteristic equivalent or combining-weight.* The atomic theory suggests at once an ideal system of equivalents or combining-weights, namely, the relative weights of the atoms themselves. If these have once been ascertained for a series of elements, the composition of all their compounds can be calculated immediately. Thus, if the atomic weights of oxygen and of carbon have been determined relatively to hydrogen, it is evident that these weights must reappear when analyses are made, not only of the compounds of carbon and oxygen with hydrogen, but also in their compounds with each other or with some fourth element such as sulphur.

Equivalents and Atomic Weights.

Many elements possess more than one equivalent, but in practice it does not matter very much which of these numbers is selected as the typical combining-weight of the element. Thus, in the case of the oxides of carbon, 8 *parts by weight of oxygen* (equivalent to 1 part of hydrogen) are united with 6 *parts by weight of carbon* in carbonic oxide, but with only 3 *parts of carbon* in carbonic anhydride. In building up a table of equivalents, it would be equally suitable to use 3 or 6 parts of carbon, although there might be some advantage in employing the smaller number. But mere analysis does not enable us to determine the actual number of atoms in the molecule, nor the

real atomic weights of the atoms even on a relative scale. Thus, the composition of the two oxides of carbon as expressed by the atomic theory may be represented equally well by two alternative pairs of symbols.

(*a*) If the relative weight of the carbon atom ● is **6**, and that of the oxygen atom ○ is **8**, then we have—

carbonic anhydride ○●○, ternary; *carbon* : *oxygen* = 6 : 16 = **3 : 8**.
carbonic oxide ●○, binary; *carbon* : *oxygen* = 6 : 8 = **3 : 4**.

(*b*) If the relative weight of the carbon atom ● is **3**, and that of the oxygen atom ○ is **8**, then—

carbonic anhydride = ●○, binary; *carbon* : *oxygen* = **3 : 8**.
carbonic oxide = ●○●, ternary; *carbon* : *oxygen* = 6 : 8 = **3 : 4**.

Using Berzelius's symbols, the two oxides of carbon may be written as follows :—

(*a*) *carbonic anhydride* = CO_2, *carbonic oxide* = CO } if C = 6 and O = 8.
(*b*) *carbonic anhydride* = CO, *carbonic oxide* = C_2O } if C = 3 and O = 8.

Dalton's rule was to select in every case the simplest series of formulæ; but he had no fixed rule to enable him to deal with doubtful cases, such as the oxides of carbon, where each system leads to one binary and one ternary formula. In practice, this particular case was settled by assigning the ternary formula to the heavier gas; carbon anhydride was therefore regarded as the ternary compound ○●○ or CO_2, and carbonic oxide as the binary compound, ●○ or CO. In this way the weight of the carbon atom was fixed at 6, where oxygen was 8 and hydrogen was 1.

No such guidance is available in the case of the two oxides of copper,

black oxide *copper* : *oxygen* = 63 : 16
red oxide *copper* : *oxygen* = 63 : 8

which may be represented in two ways, thus—

(*a*) Black oxide, CuO_2; red oxide, CuO, if O = 8 and Cu = 63.

(*b*) Black oxide, CuO; red oxide, Cu_2O, if O = 8 and Cu = 31·5.

Berzelius adopted the former hypothesis, making the black oxide a ternary compound and the red oxide binary, but was obliged to abandon it in favour of the second hypothesis.

In order to decide the actual number of atoms in the molecule, and the relative atomic weights of the elements, it is necessary to call in physical methods, which are described in detail in the following chapter. The names and symbols of the chief elements, together with modern values for their atomic weights, are, however, shown in the following table.

TABLE 9.—LIST OF PRINCIPAL ATOMIC WEIGHTS

Non-metals.			Metals.					
Hydrogen	H	= 1	Sodium	Na	= 23	Arsenic	As	= 75
Boron	B	= 11	Magnesium	Mg	= 24·3	Strontium	Sr	= 87·6
Carbon	C	= 12	Aluminium	Al	= 27	Silver	Ag	= 107·9
Nitrogen	N	= 14	Potassium	K	= 39	Cadmium	Cd	= 112·4
Oxygen	O	= 16	Calcium	Ca	= 40	Tin	Sn	= 118·7
Fluorine	F	= 19	Chromium	Cr	= 52	Antimony	Sb	= 120·2
Silicon	Si	= 28·3	Manganese	Mn	= 55	Barium	Ba	= 137·4
Phosphorus	P	= 31	Iron	Fe	= 55·8	Platinum	Pt	= 195·2
Sulphur	S	= 32	Cobalt	Co	= 59	Gold	Au	= 197·2
Chlorine	Cl	= 35·5	Nickel	Ni	= 58·7	Mercury	Hg	= 200·6
Bromine	Br	= 80	Copper	Cu	= 63·6	Lead	Pb	= 207·2
Iodine	I	= 127	Zinc	Zn	= 65·4	Bismuth	Bi	= 208

This table shows 12 non-metals and 24 metals. The atomic weights are within 0·1 of the values now adopted as exact, but 22 of them are represented by whole numbers, as they fall within ± 0·1 of an integer. A complete list of the elements with their exact atomic weights is given in Table 98, p. 907. This table also shows the serial numbers or ATOMIC NUMBERS (p. 535) of the elements when classified according to the order of their atomic weights, as described in Chapter XXXI.

SUMMARY AND SUPPLEMENT.

The Laws of Chemical Combination can be explained by means of Dalton's Atomic Theory, using the relative weights of the atoms as the equivalents or combining-weights of the elements. Where several compounds are formed there is a choice of equivalents and it is difficult to decide which of these represents the correct relative weight of the atom. Dalton therefore selected his atomic weights so as to give the simplest possible formulæ, *e.g.*, binary rather than ternary, as in the case of water = HO. Dalton's views were largely anticipated by Higgins, who failed, however, to secure general recognition for them.

CHAPTER XII

THE PROPERTIES OF GASES

The Atomic and Molecular Theories.

Dalton's atomic theory may be regarded as a *chemical* theory which serves to explain the laws of chemical combination, without giving any conclusive evidence of the size of the atoms, or even of their real existence. The molecular theory, on the other hand, by which these deficiencies have been made good, arose from an attempt to explain the *physical* properties of gases, as set out in the following paragraphs. Its fundamental theorem is generally known as " Avogadro's hypothesis," being named after the Italian physicist who brought it forward in 1811, a few years after it had been thought out and rejected by Dalton.

The Fundamental Properties of Gases and their Explanation.

(*a*) *Expansion.*—Gases differ fundamentally from liquids and solids in the power which they possess of expanding to an indefinite extent. Other substances such as rubber may be stretched considerably, but break when strained beyond a very moderate limit. The simplest explanation of the indefinite expansion of gases is that they have a *discontinuous structure*, *i.e.*, that they are made up of particles and spaces. When a gas expands, the spaces are increased, but the size of the particles is not altered substantially. These particles are usually described as MOLECULES (diminutive of Latin *moles*, a mass), and the theory that gases are made up of particles and spaces constitutes the MOLECULAR THEORY in its simplest form.

In chemistry the word " molecule " is used to describe the smallest particle in which the chemical properties of a substance are retained, whether the substance is an element or a compound, and independently of its state of aggregation as a gas, liquid, or solid. In the case of some elements the molecule consists of a single atom ; in other elements, and in all compounds, it contains more than one atom.

(*b*) *Elasticity.*—Gases possess the property of exerting a pressure in all directions. As the volume of the gas increases the pressure which it exerts is diminished, but even when very greatly attenuated the gas is

able to exert a pressure which is still approximately proportional to the greatly reduced concentration of the gas. In order to account for this pressure it is assumed that gases consist of particles in motion and that the pressure which a gas exerts is due to the bombardment of the walls of the containing vessel by the molecules of the gas. The theory that gases consist of particles in motion is called the KINETIC THEORY OF GASES (Greek κινέω, I move). As the pressure which a gas exerts does not diminish with time, it is assumed that the molecules are perfectly elastic, so that no energy is lost when the molecules collide with one another or with the walls of the containing vessel.

Influence of Pressure upon Gases. Boyle's Law.

Boyle, in 1662, discovered that when air was compressed or expanded at constant temperature, "the pressures and expansions were in reciprocal proportion." This hypothesis, which was afterwards found to apply to all gases, is now known as BOYLE'S LAW, and is stated as follows :—

> "*When the temperature is constant, the pressure of a gas varies inversely as its volume.*"

i.e., pressure × volume = constant, or pv = constant. Boyle's Law can be deduced directly from the kinetic theory of gases, since if the number of particles in a given volume be doubled, there will be twice as many impacts in a given time, and the pressure exerted on the walls of the containing vessel will also be doubled.

Deviations from Boyle's Law.—Later work has shown that Boyle's Law is only approximately true. Thus, at a pressure of 300 atmospheres both hydrogen and nitrogen occupy a volume about 25 per cent. greater than that calculated from Boyle's Law (compare Fig. 56, p. 129, where, if Boyle's Law held good, horizontal straight lines would be obtained by plotting pv against p. These deviations at high pressures can be accounted for by assuming that in a litre of gas at atmospheric pressure a volume amounting usually to one or two c.c. represents the minimum space into which particles of the gas can be compressed, and that Boyle's Law applies only to the spaces between the particles. This may be expressed in mathematical form by writing :

$$p\,(v - b) = \text{constant}$$

where $b = 0{\cdot}8$ c.c. for 1 litre of hydrogen and 2 c.c. for 1 litre of carbonic anhydride at 0° and 760 mm. pressure.

At low temperatures the mutual attraction between the particles, which ultimately leads to the liquefaction of the gas, is another disturbing factor, since it assists the external pressure in diminishing the volume of the gas. This effect is expressed satisfactorily by a term $\frac{a}{v^2}$ in the equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = \text{constant},$$

where a is a constant representing the mutual attraction between the molecules.

Influence of Temperature on Gases. Charles's Law.

It was shown by Gay-Lussac in 1802 (following some experiments made by Charles in 1787) that gases and vapours were "expanded equally by the same degrees of heat." Thus, he found that between the freezing-point and the boiling-point of water the expansions of four typical gases were as follows :—

	Expansion.	Differences.
Atmospheric air	37·50%	—
Hydrogen	37·52	+ 0·02
Oxygen	37·48	— 0·02
Azote	37·49	— 0·01

Gay-Lussac therefore concluded that all gases and all vapours were influenced in exactly the same way by changes of temperature and of pressure, a remarkable conclusion which has no parallel in the case of liquids or solids.

(*a*) *Deviations from Charles's Law.*—The influence of temperature on a gas may be shown either by an increase of pressure when the volume is constant, or by an increase of volume when the pressure is constant ; the COEFFICIENT OF EXPANSION may therefore be measured either (i) *at constant volume* or (ii) *under constant pressure.* Accurate measurements have shown that these coefficients vary slightly in different gases, as follows :—

TABLE 10.—EXPANSION OF GASES BETWEEN 0° AND 100°.

	Boiling-point.	*At Constant Volume.* Pressure.	Expansion.	*Under Constant Pressure.* Pressure.	Expansion.
Helium . .	−269°	567 mm.	0·3665	—	—
Hydrogen .	−253°	700	0·36626	—	0·36613
Nitrogen .	−196°	760	0·3668	—	—
		1002	0·36744	1002 mm.	0·36732
Argon . .	−186°	517	0·3668	—	—
Air . .	—	760	0·36650	760	0·36706
Oxygen .	−183°	759	0·36681	—	—
Carbon dioxide	− 79°†	518	0·36981	760	0·37099
		998	0·37262		
Sulphur dioxide	− 10°	760	0·38453	760	0·39028

† Sublimation-point of the solid.

These coefficients are not exactly equal, but they become more nearly so as the gas is removed from the point of liquefaction, *e.g.*, at low pressures or at high temperatures.

(*b*) *Scales of Temperature.*—The increase of pressure which takes place when a gas is heated at constant volume is attributed by the kinetic theory to a proportional increase in the kinetic energy of the molecules ; the temperature of the gas may therefore be measured either by the energy which it contains or by the pressure which it exerts. This idea finds a practical

expression in the CONSTANT VOLUME GAS THERMOMETER, in which the pressure of a gas is used to establish a standard SCALE OF TEMPERATURES. For this purpose it is necessary to select

(i) Two changes such as the freezing and boiling of water which take place abruptly at fixed temperatures, as FIXED POINTS of the scale, *e.g.*, 0° and 100° C., or 32° and 212° F.

(ii) Some property which varies continuously with temperature for use in dividing up the interval between the fixed points.

The expansion of mercury in glass is a very arbitrary choice, and has the disadvantage not only of giving a different scale from other liquids, but also of being affected substantially by the composition of the glass used in making the thermometer. For this reason, the constant volume gas thermometer is now generally used as a standard, not only for dividing up the interval between 0° and 100° C., but also for continuing the scale above and below these temperatures. The gas selected for filling the thermometer should be as nearly as possible a PERFECT GAS, *i.e.*, its deviations from the simple gas laws should be as small as possible, and in particular it should be far away from the point of liquefaction. For work at high temperatures nitrogen is generally selected; at more moderate temperatures hydrogen is used, and at the lowest temperatures helium, if necessary under reduced pressure to prevent liquefaction. In each case the scale needs a slight correction to give the ideal scale of a perfect gas, but these corrections are very small, *e.g.*, in the case of the hydrogen thermometer the correction is only + 0·06° at − 200°, − 0·0005° at 50°, and + 0·05° at 1000°.

(*c*) *The Absolute Scale of Temperatures.*—When the kinetic energy of a gas, or the square of the velocity of its particles, is taken as a measure of its temperature, there is no obvious upper limit to these quantities; but there must be a point, low down on the scale of temperature, at which the whole of the energy would be removed, and the velocity would be reduced to nothing. This point is called the ABSOLUTE ZERO of temperature. The position of the absolute zero on the Centigrade scale can be calculated by dividing into 100 the expansion of a gas between 0° and 100° C. The temperature calculated in this way will vary slightly with the coefficient of expansion of the gas, and must be corrected for the deviations from the simple gas laws, which are brought about by the mutual attraction and finite size of the particles as expressed by the constants *a* and *b* on p. 122 above. In the case of an ideal or PERFECT GAS, for which the constants *a* and *b* would be zero (so that the gas could not be liquefied by cooling or by pressure, but could be compressed indefinitely as a gas), the expansion between 0° and 100° would be 0·3661, and the absolute zero is therefore fixed at $-\frac{100}{0 \cdot 3661} = -273 \cdot 1°$. The boiling-point of helium under reduced pressure is within about 3° of this zero. As the pressure and volume of a gas are proportional to its temperature as measured from this point, it is often convenient to turn the Centigrade scale into an ABSOLUTE SCALE OF TEMPERATURE by adding 273·1° to the Centigrade readings.

Gases Unite in Simple Proportions by Volume.

In 1805, three years after his experiments on the dilation of gases and vapours by heat, Gay-Lussac made a series of accurate measurements

of the combining volumes of hydrogen and oxygen. It was already known that these gases united in the ratio 2 : 1 approximately; the measurements of Gay-Lussac showed that 100 parts of oxygen united with 199·89 parts of hydrogen, a number that agreed remarkably closely with the integral ratio 1 : 2.*

Gay-Lussac was able to detect similar relationships in the combining volumes of many other gases. Thus, nitrogen and hydrogen in ammonia are united in the ratio 100 : 300, whilst in the three gaseous oxides of nitrogen 100 volumes of nitrogen are united with 50, 100, and 200 volumes of oxygen. The actual analyses showed small deviations from these exact ratios, but Gay-Lussac regarded these as due to experimental errors and was able to prove in certain cases that more careful analyses gave numbers agreeing more closely with those required for exact integral ratios.

Gaseous Products are Formed in Simple Proportions by Volume.

Gay-Lussac showed, further, that simple ratios existed between the volumes of gases used in a chemical change and the volumes of the gases produced. Thus, when charcoal and sulphur are burnt in air, no marked change in volume takes place, because *one volume of oxygen* yields *one volume of carbonic anhydride* or *one volume of sulphurous anhydride.* Again, *one volume of nitrogen* and *three volumes of hydrogen* yield *two volumes of ammonia,* whilst *one volume of nitrogen* and *one volume of oxygen* yield *two volumes of nitric oxide.*

Gay-Lussac's Law of Volumes.

Gay-Lussac's LAW OF VOLUMES, which covers all these various cases, may be expressed as follows :—

> "*When gases enter or leave chemical combination, the volumes absorbed, or liberated, are in simple ratios to one another.*"

Gay-Lussac was much impressed by the fact that these simple ratios are not observed in solid or liquid substances, nor when weights are considered instead of volumes. He concluded that gases must possess a very simple structure, and directed attention to the fact that the behaviour of gases could be interpreted most easily with the help of the atomic theory which Dalton had recently formulated.

Gay-Lussac's Law of Volumes only Approximately True.

It is now recognised that Gay-Lussac's law of volumes is not exact. Thus, hydrogen and oxygen unite together in the ratio 2·00245 : 1 at the atmospheric temperature. Hydrogen and nitrogen unite in the ratio of 3·00172 : 1. Again, the volume of hydrogen contained in the two volumes of hydrogen chloride is not 1 but 1·0079. These deviations

* Gay-Lussac's ratio differs in the wrong direction from the integral ratio 2 : 1, the actual combining volumes being in the ratio 100 : 200·24.

depend on the fact that gases differ slightly in compressibility and deviate to different extents from the requirements of Boyle's law. It is believed that Gay-Lussac's law would be rigidly true at very low pressures; when, however, the pressure is increased, hydrogen (which is slightly less compressible than other gases) maintains a volume slightly larger than Gay-Lussac's law would require.

Mixtures of Gases.

Gases possess the property of mixing freely in all proportions. Each gas tends to distribute itself throughout the containing vessel just as if no other gas were present, and the properties of the mixture are the sum of the properties of the constituents. Thus, the atmosphere is usually said to consist of one-fifth of oxygen and four-fifths of nitrogen by volume; but a more exact statement is that a litre of air under atmospheric pressure contains a litre of oxygen under a partial pressure of one-fifth of an atmosphere and a litre of nitrogen under a partial pressure of four-fifths of an atmosphere.

Under ordinary conditions gases "diffuse" into one another until the composition is uniform throughout, *the rate of diffusion varying inversely as the square root of the density* (GRAHAM'S LAW) (compare p. 15); but as gases differ slightly in their compressibility, especially at low temperatures, there is a tendency for the compressible gases in the atmosphere to accumulate in the lower layers, and for the less compressible gases to predominate in the upper layers. Thus, Dewar has calculated that at the height of 37 miles the proportion of oxygen would be reduced from 21 per cent. to 10 per cent., and that the hydrogen, which amounts only to 0·02 per cent. at the surface, would rise to 12 per cent. at this height; at a height of 47 miles, the nitrogen and oxygen would practically disappear and hydrogen would be almost the only common gas remaining. Similar considerations make it plausible to admit the possibility of separating gases into their more compressible and less compressible constituents by the action of centrifugal force.

SUMMARY AND SUPPLEMENT.

1. **The Kinetic Theory of Gases** assumes that gases are composed of particles in motion, and that the pressure which they exert is due to the incessant bombardment of the walls of the containing vessel by these particles.

(*a*) *Pressure.*—The pressure, p, exerted by the particles, *e.g.*, in a cubical container, is proportional to their number, their mass, and the square of their velocity, and inversely proportional to the volume occupied, the numerical relationship being given by the equation

$$pv = \tfrac{1}{3}\, nmc^2 .$$

where n is the total number of particles in volume v, m is the mass of each particle, and c is the mean "squared" velocity.*

* *i.e.*, $nc^2 = c_1^2 + c_2^2 + \ldots + c_n^2$ instead of $nc = c_1 + c_2 + \ldots + c_n$

Since $\frac{1}{2}nmc^2$ represents the total kinetic energy (*K.E.*) of the particles, it follows that $pv = \frac{2}{3}(K.E.)$, *i.e.*, the product of pressure and volume is constant so long as the energy remains constant (*Boyle's Law*).

(*b*) *Temperature.*—The average kinetic energy of the particles is taken as a measure of the temperature of a gas. We may therefore write

$$pv = \tfrac{2}{3}(K.E.) = RT$$

where R is a constant. The temperature, T, may be measured either by the pressure which the gas exerts when the volume is constant (constant volume gas thermometer) or by its volume when the pressure is constant (constant pressure gas thermometer.) This is in harmony with *Charles's Law*, which states that the volume of a gas increases when its temperature is raised, and in the same ratio for all gases. The temperature of a gas can be increased indefinitely, but diminishes to an ABSOLUTE ZERO, when all its energy is removed and the particles are at rest.

This absolute zero is fixed at $-273 \cdot 1°$ on the Centigrade scale, since the normal coefficient of expansion of a gas between 0° and 100° is 0·3661 and $\frac{100}{0 \cdot 3661} = 273 \cdot 1°$. The pressure or volume of a gas is proportional to its ABSOLUTE TEMPERATURE as measured from this point, thus, it increases in the ratio 273 to 373 between the freezing-point and boiling-point of water.

(*c*) *Number of Particles.*—Two gases are at the same temperature when the average kinetic energy of the particles is the same in both, *i.e.*, when

$$\tfrac{1}{2}m_1c_1^2 = \tfrac{1}{2}m_2c_2^2,$$

where m_1, c_1 are the mass and velocity of the particles in the first gas, and m_2, c_2 are the corresponding quantities for the second gas. If the pressure and volume are also the same in the two gases, *i.e.*, if $p_1v_1 = p_2v_2$, then

$$\tfrac{1}{2}n_1m_1c_1^2 = \tfrac{1}{2}n_2m_2c_2^2.$$

Combining these two equations, we find that

$$n_1 = n_2,$$

i.e., equal volumes of different gases contain equal numbers of molecules when the temperature and pressure are the same (*Avogadro's Hypothesis*).

The actual number of particles in 1 litre of gas at 0° and 760·mm. pressure has been determined by several widely different methods to be $n = 3 \times 10^{22}$.

(*d*) *Mean Velocity of Particles.*—The mean squared velocity of the particles is given by

$$c^2 = \frac{3\,pv}{mn}.$$

Writing $\frac{mn}{v} = d$ (density), we have

$$c^2 = \frac{3\,p}{d}.$$

The mean velocities of the particles of different gases when exerting equal pressures are therefore inversely proportional to the square roots of the densities, *e.g.*, four times as great in hydrogen as in oxygen, which is sixteen times as dense (*Graham's Law of Diffusion*).

The density of oxygen is 1·42900 grams per litre or 0·001429 gram per c.c. at 0° under a pressure of 760 mm. of mercury, *i.e.*, of $76 \times 13 \cdot 60 \times 981 =$ 1,013,000 dynes per sq. cm. The mean squared velocity, c, of the particles is therefore $\sqrt{\frac{3 \times 1{,}013{,}000}{0 \cdot 001429}} = 46{,}100$ cm. (or about 0·3 mile) per second

at 0°. For hydrogen the velocity is four times greater, *i.e.*, 192,000 cm. (or about 1·2 miles) per second at 0°. The squares of these velocities increase proportionally with the temperature as measured from $-273°$.

(e) *Energy.*—The energy of the gas is given by the equation

$$K.E. = \tfrac{3}{2}\,pv = \tfrac{3}{2}\,RT.$$

The increase of kinetic energy per degree, when no external work is done, *i.e.*, when the gas is heated at constant volume, is

$$\frac{K.E.}{T} = \tfrac{3}{2}\,\frac{pv}{T} = \tfrac{3}{2}\,R.$$

When, however, the gas is heated at constant pressure and allowed to expand, it also does external work represented by the product of pressure into increase of volume, *i.e.*,

$$p\,\frac{v}{T} = R,$$

and the total energy absorbed is increased to $\tfrac{5}{2}\,R$.

Taking the molecular weight of oxygen, as deduced on p. 136, to be 32, we find that for 32 grams of oxygen, $v = 22{\cdot}4$ litres or 22,400 c.c. when $p =$ 1 atmosphere or 1,013,000 dynes and $T = 0°$ C. or 273° absolute.

$$\therefore \quad R = \frac{pv}{T} = \frac{1{,}013{,}000 \times 22400}{273}\ \text{ergs}$$

$$= \frac{1{,}013{,}000 \times 22400}{273 \times 41{,}890{,}000}\ \text{calories (since 1 calorie} = 41{,}890{,}000\ \text{ergs)}$$

$$= 1{\cdot}985,\ \text{or 2 calories approximately, for 1 "gram-molecule" of gas.}$$

For an ideal gas, in which all the energy absorbed goes to increase the velocity, *c*, of the particles, the MOLECULAR HEAT AT CONSTANT VOLUME (p. 140) is $\tfrac{3}{2}R=3$ and the MOLECULAR HEAT AT CONSTANT PRESSURE is $\tfrac{5}{2}R=5$ calories. These figures are substantially correct for "monatomic" gases, but when the molecule contains two or more atoms much energy is absorbed in producing rotation or "spin" in the molecules and higher values are observed (p. 140).

2. Perfect and Imperfect Gases.—The preceding calculations refer to an ideal or PERFECT GAS, composed of infinitely small particles having no mutual attraction for one another. Such a gas could be compressed indefinitely, in accordance with Boyle's law, and could also be cooled to any extent, without separating into liquid and vapour. Actual gases deviate from this ideal in two ways :

(i) There is a minimum volume *b*, which is a function of the volume of the particles, beyond which they cannot be compressed, so that Boyle's law applies only to the empty space, $v - b$, between them.

(ii) The particles have an attraction for one another which appears to vary inversely as the square of the volume and is expressed by the constant *a* in the EQUATION OF STATE of Van der Waals,

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.$$

The imperfection of actual gases is shown primarily by the fact that they cannot be compressed indefinitely and that they liquefy under the influence of cooling and compression. There are, however, many points in which the imperfection shows itself in a less dramatic way in the form of deviations from the simple GAS LAWS of an ideal gas. Thus we find :

(*a*) *Deviations from Boyle's Law.*—These are shown in Fig. 56 by plotting pv against p, when a horizontal straight line should result. Actually, hydrogen is less compressible, whilst nitrogen is at first more compressible than Boyle's law would indicate, but finally becomes less compressible as the b factor predominates over a. At 300 atmospheres the deviation is 25 per cent. both for hydrogen and for nitrogen. The conversion of the horizontal into a vertical straight line during liquefaction is shown in the isotherm for carbon dioxide.

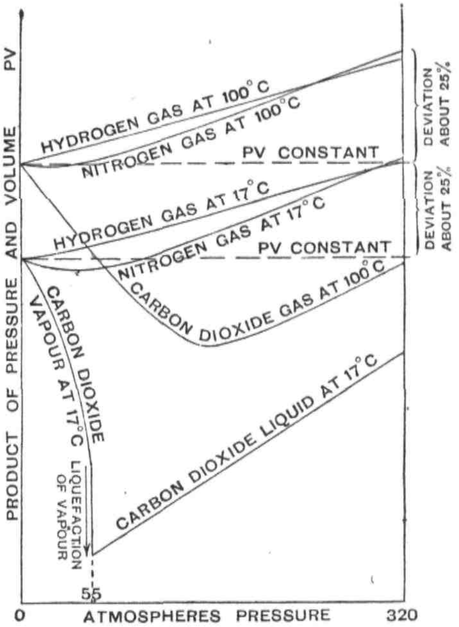


FIG. 56.—DEVIATIONS FROM BOYLE'S LAW.

(*b*) *Deviations from Gay-Lussac's Law of Volumes.*—If equal volumes of different gases be taken at very low pressures their volumes will become unequal at atmospheric pressure in the inverse ratio of the factor $1 + \lambda = (1 + a)(1 - b)$, where λ is a constant which expresses the combined effect of the terms a and b. The relative volumes of some common gases when thus brought from zero to 760 mm. pressure at 0° are as follows:

TABLE 11.—RELATIVE VOLUMES OF GASES.

	λ.	*Relative volumes.*
Helium . . .	− 0·00013	1·00013
Hydrogen . .	− 0·00062	1·00062
Nitrogen . .	+ 0·00051	0·99949
Oxygen . . .	+ 0·00075	0·99925
Carbon monoxide .	+ 0·00077	0·99923
Carbon dioxide .	+ 0·00682	0·99322
Sulphur dioxide .	+ 0·02601	0·97465

It is to these ratios, rather than to equal volumes, that Gay-Lussac's Law of Volumes applies, *e.g.*, the combining volumes of hydrogen and oxygen are in the ratio $\frac{2 \times 1{\cdot}00062}{1 - 0{\cdot}00075} = 2 \times 1{\cdot}00137$ to 1.

Similar corrections are needed in applying Avogadro's Hypothesis to deduce molecular weights from the densities of gases (p. 141).

(*c*) *Internal Work.*—When a perfect gas expands from pressure p_1, volume

v_1, to pressure p_2, volume v_2, without doing external work (*e.g.*, by expanding into a vacuum),

$$p_2v_2 = p_1v_1,$$

and the energy and temperature of the gas which are measured by this product are unchanged by the expansion. In the case of actual gases, however, this equation is no longer valid, since in expanding, *e.g.*, from 1 atmosphere to zero pressure the product increases in the ratio $1 : 1 + \lambda$. This has the effect of heating gases such as helium and hydrogen for which λ is negative ($pv > p_0v_0$ or $a < b$), but of cooling all gases for which λ is positive

$$(pv < p_0v_0 \text{ or } a > b).$$

The magnitude of this cooling (*Joule-Thomson effect*) for some common gases under moderate pressures is, for 1 atmosphere expansion at 0°, as follows:

TABLE 12.—COOLING OF GASES BY EXPANSION.

Carbon dioxide . . .	1·46°
Oxygen	0·326°
Nitrogen	0·31°
Hydrogen	− 0·03°

The cooling increases as the temperature falls, and decreases and becomes negative as the temperature rises; the temperature at which the change of sign takes place is described as the "temperature of inversion of the Joule-Thomson effect."

The cooling, due to internal work done against the mutual attraction of the molecules, is used in the Linde process (p. 371) to liquefy air by expansion from a nozzle. In the case of hydrogen the gas is first cooled with liquid air, to produce a cooling effect on expansion, and for the same reason helium is cooled with liquid hydrogen before allowing it to expand.

3. **Liquefaction.**—Van der Waals's equation covers the process of liquefaction. Thus, when the relationship between pressure and volume is plotted as a series of isotherms for different values of T, the curves shown in Fig. 57 for the typical case of carbonic anhydride are obtained.

(*a*) The isotherm AB for 100° is approximately a rectangular hyperbola, as required by Boyle's Law, pv = constant.

(*b*) At − 50°, however, a looped curve, $FGHJKLM$, is obtained in which

(i) FG represents the compression of the unsaturated vapour up to the point G at which liquefaction would usually occur.

(ii) GH represents the compression of vapour which should have condensed to liquid but has persisted in a metastable condition.

(iii) HJ represents an unstable region in which pressure and volume would increase and decrease together, so that compression would result in expansion!

(iv) JK represents liquid under tension, a phenomenon which can actually be realised as a metastable condition in some liquids.

(v) KL represents liquid which should have vaporised under these low pressures but has persisted in a metastable state.

(vi) LM represents the normal compression of the liquid.

The metastable condition of supersaturated vapour (ii) can be realised by cooling a vapour which is quite free from dust, *e.g.*, by expanding it, to a temperature much below that at which a cloud of liquid drops would usually

appear. The metastable liquid state (v) can be realised by heating an air-free liquid above its normal boiling-point, as always occurs, for instance, when a liquid "bumps" during boiling. The metastable state of liquid under tension (iv) can be realised by warming air-free liquid in a sealed tube until it just fills the tube and then letting it cool. Usually, however, the loop

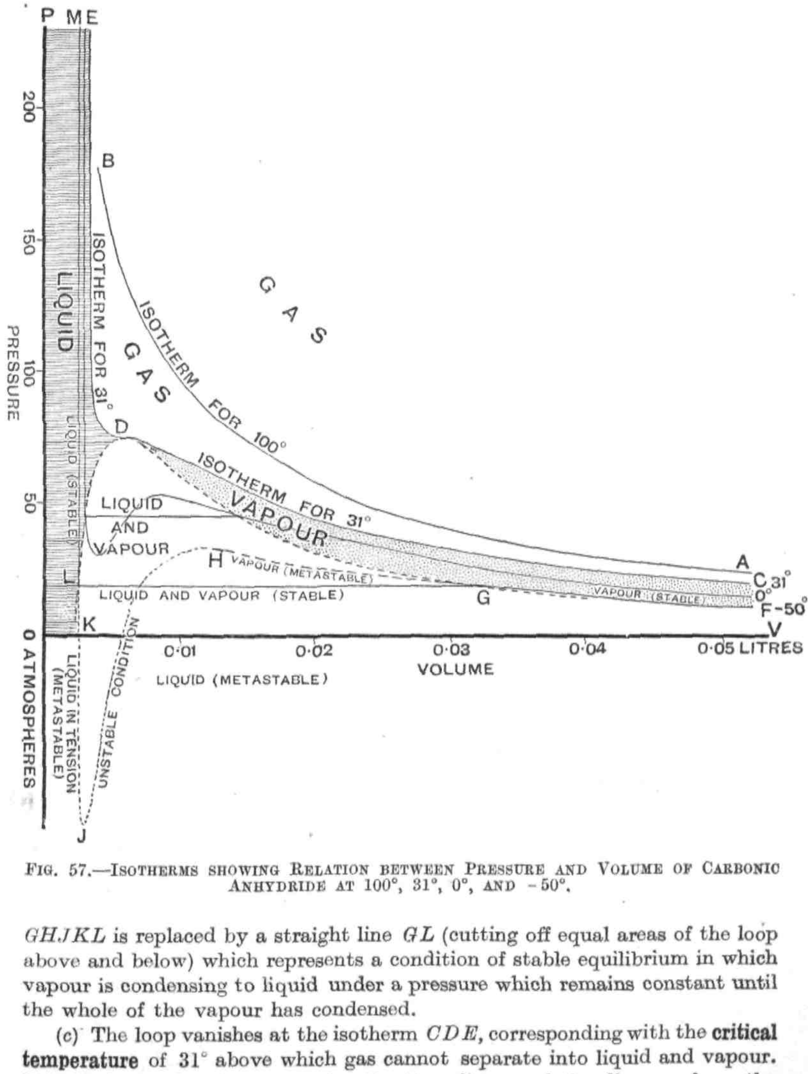


FIG. 57.—ISOTHERMS SHOWING RELATION BETWEEN PRESSURE AND VOLUME OF CARBONIC ANHYDRIDE AT 100°, 31°, 0°, AND −50°.

GHJKL is replaced by a straight line *GL* (cutting off equal areas of the loop above and below) which represents a condition of stable equilibrium in which vapour is condensing to liquid under a pressure which remains constant until the whole of the vapour has condensed.

(c) The loop vanishes at the isotherm *CDE*, corresponding with the **critical temperature** of 31° above which gas cannot separate into liquid and vapour. This isotherm therefore separates the "gas" area of the diagram from the "vapour" and "liquid" areas. It can be shown that the critical constants

of a substance, which are the co-ordinates of the **critical point** D, are related to the constants of Van der Waals's equation as follows :—

$$\text{Critical volume} = 3b$$

$$\text{Critical pressure} = \frac{a}{27b^2}.$$

$$\text{Critical temperature} = \frac{8a}{27b} \times \frac{1}{R}.$$

4. The Kinetic Theory of Liquids.

(*a*) In a liquid, the mutual attraction of the particles, as represented by the term a/v^2 in Van der Waals's equation, is sufficient to hold the molecules together so that they occupy only a portion of the available space. Within the liquid, this attraction is equal in all directions, and the molecules are therefore free to travel through it on a zig-zag path, although the "free path" (*i.e.*, the distance one molecule can travel before striking another) is much smaller than in a gas. At the surface the attraction acts only in an inward direction, and is sufficiently strong to retain the majority of the molecules. A few molecules, travelling with more than the average velocity, are, however, able to escape by evaporation, and this proportion increases very rapidly as the average velocity is increased by rise of temperature. When the vapour is allowed to accumulate above the liquid, evaporation continues only until a condition of equilibrium is established in which evaporation is exactly balanced by condensation, *i.e.*, by the retention in the liquid of molecules impinging on it from the vapour. The pressure at which equilibrium is reached is called the VAPOUR PRESSURE OF THE LIQUID.

(*b*) The molecules that escape carry with them more than an average amount of energy ; the temperature of the liquid is, therefore, lowered by evaporation. The loss of energy by evaporation is measured quantitatively as the LATENT HEAT OF VAPORISATION of the liquid.

(*c*) The mutual attraction of the particles in the liquid resists any increase in its surface. It therefore gives rise to the phenomena of SURFACE TENSION, as seen in the pressure required to expand a soap bubble, in the rise of water in a capillary tube which is wetted by the liquid, and in the suspension of a drop on a dripping nozzle. The molecular weight of a liquid can be deduced from the rate at which its surface tension varies with the temperature.

CHAPTER XIII

AVOGADRO'S HYPOTHESIS

Dalton's Theory of the Equal Spacing of Particles in Gases.

The simple laws governing the influence on gases of changes of temperature, pressure, and chemical composition are best explained by supposing that the particles of different gases, although differing in size and weight, are spaced out equally when the temperature and pressure are the same. This theory was put forward in 1802 by Dalton, who adopted the view that the spaces occupied by the ultimate particles of "elastic fluids" or gases are all equal, so that a given volume of oxygen gas contains the same number of particles as an equal volume of hydrogen gas, and so forth.

This idea was rejected by Dalton on the following grounds. If it be assumed that the ultimate particles of nitrogen, oxygen, and nitric oxide all occupy equal volumes, it is evident that the combination of a particle of nitrogen with a particle of oxygen must be accompanied by a decrease of volume, since the number of particles is reduced by combination; and further that the density of the gas must be increased thereby. Actually, Davy had shown that this combination was not accompanied by any change of volume, and that the density of nitric oxide was intermediate between those of nitrogen and oxygen, and therefore actually less than that of the oxygen which was one of its constituents. These facts were completely at variance with his theory as to the spacing of the particles, and Dalton was obliged to discard the simple views which he had adopted to account for the simple properties of gases.

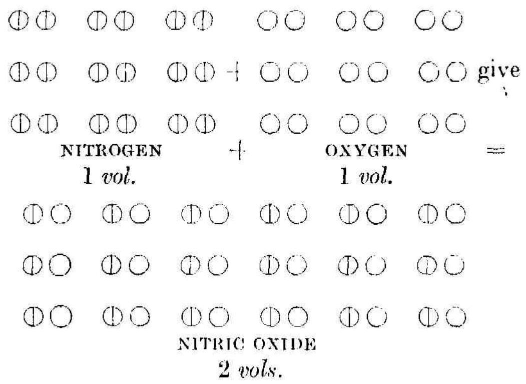
Avogadro's Hypothesis.

Dalton's theory was revived in 1811 by the Italian physicist Avogadro. AVOGADRO'S HYPOTHESIS, as it is now generally called, states that—

> "*When the temperatures and pressures are the same, equal volumes of different gases contain equal numbers of molecules.*"

The difficulty which Dalton had found in applying this hypothesis was removed when Avogadro suggested that the molecules of an elementary gas might consist of groups of similar atoms, corresponding

precisely with the groups of dissimilar atoms which form the molecules of a compound gas. Thus, if the molecules of nitrogen and oxygen as well as those of nitric oxide were assumed to contain two atoms each, there need be *no* change of volume and *no* change of density when a mixture of nitrogen and oxygen was converted into nitric oxide. This may be shown by means of the following diagrams :—



The chemical change is here represented, not as a direct combination of atoms of nitrogen with atoms of oxygen, but rather as a double decomposition in which an interchange of atoms takes place between complex molecules of the two elements.

Subdivision of the Gaseous Molecule.

The most obvious application of Avogadro's hypothesis is found in interpreting the chemical changes in gases which were described by Gay-Lussac in setting forth his law of volumes. In each case we may, in accordance with Avogadro's hypothesis, substitute "molecules" for "volumes" in the equations and so secure information as to the molecular changes underlying these actions. Thus, the experimental equations

carbon	+ oxygen 1 *vol.*	= carbonic anhydride 1 *vol.*
sulphur	+ oxygen 1 *vol.*	= sulphurous anhydride 1 *vol.*

which show the volumes of the gases concerned in the burning of carbon and sulphur in air, may be rewritten to show the molecular changes as follows :—

carbon	+ oxygen 1 *mol.*	= carbonic anhydride 1 *mol.*
sulphur	+ oxygen 1 *mol.*	= sulphurous anhydride 1 *mol.*

In the same way, the composition of nitric oxide and of muriatic acid may be represented by the equations :

nitrogen +	oxygen	= nitric oxide
1 *vol.*	1 *vol.*	2 *vols.*
1 *mol.*	1 *mol.*	2 *mols.*

hydrogen +	chlorine	= hydrogen chloride
1 *vol.*	1 *vol.*	2 *vols.*
1 *mol.*	1 *mol.*	2 *mols.*

The formation of water and the decomposition of ammonia are represented by the equations :—

hydrogen +	oxygen	= water (gaseous)
2 *vols.*	1 *vol.*	2 *vols.*
2 *mols.*	1 *mol.*	2 *mols.*

ammonia =	hydrogen	+ nitrogen
2 *vols.*	3 *vols.*	1 *vol.*
2 *mols.*	3 *mols.*	1 *mol.*

From these equations the complexity of the molecules of the four gaseous elements can be determined as follows :—

(*a*) *Hydrogen.*—It is seen that no subdivision of the hydrogen molecule takes place when hydrogen is converted into steam ; but that when hydrogen is converted into hydrogen chloride the molecule of hydrogen is divided into two parts, and distributed between two molecules of hydrogen chloride ; one hydrogen-molecule is also divided into two parts when three molecules of hydrogen are used to produce two molecules of ammonia. In the absence of any evidence of further subdivision of the hydrogen-molecule, we may therefore assume that the *half-molecule of hydrogen is the atom*, or, conversely, that *the molecule of hydrogen is composed of two atoms*, and may be represented by the formula H_2.

(*b*) *Oxygen.*—No subdivision of the oxygen molecule takes place when it is united with carbon or with sulphur ; but when oxygen unites with hydrogen to form steam or with nitrogen to form nitric oxide each molecule of oxygen yields 2 molecules of the product and is therefore subdivided into two parts. Since no further subdivision is observed, it may be assumed that *the atom of oxygen is the half-molecule*, or, conversely, that *the molecule of oxygen is composed of two atoms*, and may be represented by the formula O_2.

(*c*) *Nitrogen.*—In just the same way it is seen that a molecule of nitrogen is divided into two parts when it combines with oxygen to form nitric oxide, or with hydrogen to form ammonia. The *molecule of nitrogen may therefore be assumed to contain two atoms* as represented by the formula N_2.

(*d*) *Chlorine.*—In combining with hydrogen to form hydrogen chloride, *the molecule of chlorine is divided into two parts* ; *the molecule*

is therefore assumed to contain two atoms and is represented by the formula Cl_2.

Monatomic, Diatomic, and Polyatomic Molecules.

In the case of these four elements, a study of all the compounds to which Avogadro's method can be applied confirms the conclusion that the gaseous molecules are composed of two atoms and cannot be subdivided further; the molecules are therefore said to be DIATOMIC. In other cases, however, the gaseous molecule is found to be MONATOMIC, that is, it is composed of a single atom and is not divisible by ordinary chemical methods, *e.g.*, the molecules of zinc, cadmium, mercury, and argon are monatomic and are represented by the simple atomic symbols Zn, Cd, Hg, A. On the other hand, more complex molecules, TRIATOMIC, TETRATOMIC, or POLYATOMIC, are known, such as O_3 (ozone), P_4, As_4, S_8.

Diatomic molecules, although frequent amongst the commoner gases, are by no means universal, and in a full table of volatile elements are seen to be less abundant than the monatomic molecules.

Monatomic	Na, K, Ag, Zn, Cd, Hg, He, Ne, A, Kr, Xe, I, S, Sb.
Diatomic	H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2, S_2, As_2, Sb_2.
Polyatomic	O_3, P_4, As_4, S_8.

There is therefore no justification for the view that atoms cannot exist alone and must combine together to form molecules.

Atomic Weights of Gases deduced by Avogadro's Hypothesis.

By means of the formulæ given above for the principal gaseous elements it is possible at once to check the atomic weights assigned to them by Dalton's atomic theory. Thus, since the densities of the gases are approximately in the ratio

Hydrogen	Nitrogen	Oxygen	Phosphorus	Chlorine	Mercury
1	14	16	62	$35\frac{1}{2}$	100

and the formulæ are

H_2	N_2	O_2	P_4	Cl_2	Hg,

we may take the atomic weight of hydrogen as H = 1 and its molecular weight as $H_2 = 2$ and write down the molecular weights of these elements in round numbers as

2	28	32	124	71	200;

the atomic weights are then

$\frac{2}{2}$	$\frac{28}{2}$	$\frac{32}{2}$	$\frac{124}{4}$	$\frac{71}{2}$	$\frac{200}{1}$

or

H = 1	N = 14	O = 16	P = 31	Cl = $35\frac{1}{2}$	Hg = 200

It will be noticed at once that these atomic weights do not always agree with the combining-weights (or equivalents) of the elements, which Dalton took to represent the relative weights of the atoms, but are frequently multiples of these numbers. The factor by which the equivalent or combining-weight must be multiplied in order to give the true atomic weight is known as the VALENCY of the element, thus,

$$equivalent \times valency = atomic\ weight.$$

For the six elements discussed above these quantities are as follows :—

	Hydrogen.	Nitrogen.	Oxygen.	Phosphorus.	Chlorine.	Mercury.
Equivalent .	1	$4\frac{2}{3}$	8	$10\frac{1}{3}$	$35\frac{1}{2}$	100
Valency .	1	3	2	3	1	2
Atomic weight	1	14	16	31	$35\frac{1}{2}$	200

Calculation of Exact Atomic Weights.

The determination of *exact* atomic weights by means of Avogadro's hypothesis by the method described in the preceding paragraph is difficult (i) because exact measurements of the densities of gases and vapours are not easy to make, and (ii) because Avogadro's hypothesis is only exact at very low pressures. Thus even the most exact measurements of density made at atmospheric pressures must be corrected to allow for the unequal compressibilities of the different gases (see below, p. 142).

The ordinary method of determining exact atomic weights is, therefore, based on a modification of this method, and involves :

(i) A very exact determination of the EQUIVALENT of the element as given by careful analyses of the oxide, chloride, etc.

(ii) A determination of the VALENCY of the element, that is, of the factor by which the equivalent must be multiplied in order to give the atomic weight.

The valency is usually a simple integral number, *e.g.*, 1, 2, 3, or 4,* and only very rough measurements are needed to give a correct value for this number. In order to convert the round numbers of the preceding paragraph into exact atomic weights, therefore, the valency is taken as the integer nearest to the experimental ratio

$$\frac{approximate\ atomic\ weight}{equivalent}$$

and the exact atomic weight is obtained by multiplying the equivalent by this integer, as indicated in the following table.

* As defined above, it may also be a simple fraction, *e.g.*, the weight of iron combined with 8 parts of oxygen in the magnetic oxide must be multiplied by 8/3 to give the atomic weight of iron.

TABLE 13.—CALCULATION OF VALENCIES AND EXACT ATOMIC WEIGHTS.

Element.	Equivalent.	Approximate atomic weight.	Valency.	Exact atomic weight.
Hydrogen	1·008	about 1	1	1·008 × 1 = 1·008
Oxygen	8	16	2	8 × 2 = 16
Carbon	3·00 (in carbonic anhydride)	about 12	4	3·00 × 4 = 12·00
,,	6·00 (in carbonic oxide)	about 12	2	6·00 × 2 = 12·00
Chlorine	35·457	about $35\frac{1}{2}$	1	35·457 × 1 = 35·457

Formulæ of Gases deduced by Avogadro's Hypothesis.

Avogadro's hypothesis makes it possible not only to determine the atomic weights of the gaseous or volatile elements, but also to deduce from these the formulæ of their compounds. The method by which correct formulæ are arrived at may be shown for a number of typical cases as follows :—

(*a*) *Steam* is formed by the explosion of hydrogen and oxygen as follows :

	hydrogen	+	oxygen	=	steam	
	2 *vols.*		1 *vol.*		2 *vols.*	(by experiment)
	2 *mols.*		1 *mol.*		2 *mols.*	(by Avogadro's hypothesis)
∴	4 *atoms*	+	2 *atoms*	=	2 *mols.*	(since hydrogen and oxygen are diatomic)
or	2 *atoms*	+	1 *atom*	=	1 *mol.*	

The molecule of steam thus contains two atoms of hydrogen and one atom of oxygen and is represented by the formula H_2O, instead of by the formula HO given by Dalton's simple rules.

(*b*) *Ammonia* is decomposed by sparking as follows :

	ammonia	=	hydrogen	+	nitrogen	
	2 *vols.*		3 *vols.*		1 *vol.*	(by experiment)
	2 *mols.*		3 *mols.*		1 *mol.*	(by Avogadro's hypothesis)
∴	2 *mols.*	=	6 *atoms*	+	2 *atoms*	(since hydrogen and nitrogen are diatomic)
or	1 *mol.*	=	3 *atoms*	+	1 *atom.*	

The molecule of ammonia thus contains three atoms of hydrogen and one atom of nitrogen and is represented by the formula NH_3.

It must be emphasised that Avogadro's hypothesis only enables us to pass from *volumes* to *molecules*, and not directly from volumes to *atoms*. The fact that water is composed of hydrogen and oxygen in the ratio of two volumes to one volume does not prove by itself that the formula of water is H_2O ; the coincidence between the number of atoms of hydrogen and oxygen in the molecule of steam and the com-

bining volumes of these two gases is a mere accident depending on the fact that hydrogen and oxygen are both diatomic gases. A similar statement may be made in reference to ammonia.

The danger of omitting the intermediate step in the sequence *volumes, molecules, atoms* may be illustrated by two cases in which molecules containing unequal numbers of atoms are involved in the same equation, *e.g.*, phosphine and corrosive sublimate.

(*c*) ***Phosphine*** (p. 424) can be decomposed at high temperatures as shown in the following equations :—

	phosphine	=	phosphorus	+	hydrogen	
	4 *vols.*		1 *vol.*		6 *vols.*	(by experiment)
	4 *mols.*		1 *mol.*		6 *mols.*	(by Avogadro's hypothesis)
∴	4 *mols.*	=	4 *atoms*	+	12 *atoms*	(since the molecules are P_4 and H_2)
or	1 *mol.*	=	1 *atom*	+	3 *atoms.*	

The formula of phosphine is therefore PH_3. In this case the volumes of phosphorus and of hydrogen are in the ratio 1 : 6, but it would be incorrect to suppose that the formula of phosphine is therefore PH_6.

(*d*) The composition of *corrosive sublimate* (p. 882) as a vapour may be represented by the equation :—

	corrosive sublimate	=	mercury	+	chlorine	
	1 *vol.*		1 *vol.*		1 *vol.*	(by experiment)
	1 *mol.*		1 *mol.*		1 *mol.*	(by Avogadro's hypothesis)
∴	1 *mol.*	=	1 *atom*	+	2 *atoms*	(since the molecules are Hg and Cl_2).

The formula of corrosive sublimate is therefore $HgCl_2$ and not HgCl, although the volumes of mercury vapour and chlorine are in the ratio of 1 : 1.

Equations deduced by Avogadro's Hypothesis.

By means of Avogadro's hypothesis it is also possible (when the materials used and the products formed are all gaseous) to deduce a CHEMICAL EQUATION showing how the atoms are distributed before and after the chemical change. Thus :

(*a*) The combination of the common diatomic gases may be represented by the equations :—

N_2	+	O_2	=	2NO
1 *vol.*		1 *vol.*		2 *vols.*
H_2	+	Cl_2	=	2HCl
1 *vol.*		1 *vol.*		2 *vols.*
$2H_2$	+	O_2	=	$2H_2O$
2 *vols.*		1 *vol.*		2 *vols.*
$3H_2$	+	N_2	=	$2NH_3$
3 *vols.*		1 *vol.*		2 *vols.*

(*b*) The formation of phosphine and of corrosive sublimate from their elements may be represented by the equations :—

P_4	+	$6H_2$	=	$4PH_3$
1 *vol.*		6 *vols.*		4 *vols.*
Hg	+	Cl_2	=	$HgCl_2$
1 *vol.*		1 *vol.*		1 *vol.*

Avogadro's Hypothesis confirmed by Measurements of Molecular Heats of Gases.

Indirect evidence of the complexity of the molecules of gaseous elements is obtained from a study of their MOLECULAR HEATS, *i.e.*, the heat-capacity of 1 gram-molecule of the gas or the number of calories required to raise the temperature of M grams of the gas through 1° C., where M is the molecular weight of the gas. The evidence obtained in this way confirms the conclusions arrived at by using Avogadro's hypothesis.

On theoretical grounds, the molecular heat of an ideal gas is calculated (compare p. 128) to be 3 calories when the volume of the gas is constant, and 5 calories when the gas is allowed to expand at constant pressure, since 2 calories are absorbed in driving back the atmospheric pressure. Direct measurements of the heat-capacity of gases are difficult to make, but the ratio of the two molecular heats can be determined readily, *e.g.*, by Kundt's method, which depends on measuring the velocity of sound in the gas in a simple apparatus. From this ratio the two molecular heats can be calculated by assuming a constant difference of 2 calories between the two molecular heats. In a number of typical cases the values deduced in this way are as follows :—

TABLE 14.—MOLECULAR HEATS OF GASES.

Formula of substance and ratio of molecular heats.						Mean ratio.	Molecular heats. Const. press.	Const. vol.
A	1·666	Hg	1·667	He	1·63	1·66	5	3
H_2	1·41	O_2	1·40	N_2	1·40			
HCl	1·39	HBr	1·42	HI	1·40	1·40	7	5
CO	1·40							
Cl_2	1·34	Br_2	1·29	I_2	1·30			
H_2O	1·34	N_2O	1·32	CO_2	1·31	1·33	8	6
SH_2	1·34	NH_3	1·32	CH_4	1·31			
SO_2	1·26	CS_2	1·22	CH_3Cl	1·28	1·25	10	8
C_2H_2	1·26	C_2H_4	1·25	C_2H_6	1·22			

It will be seen that the ratios and the molecular heats fall into a series of groups. Thus, mercury, argon, and helium give practically the theoretical values 1·67 for the ratio and 5 and 3 for the molecular heats. The majority of the diatomic gases, whether simple or compound, give a ratio 1·4, and molecular heats two units higher at 7 and 5 respectively. The remaining diatomic gases and the lighter triatomic gases, together with ammonia and

marsh gas, give a mean ratio 1·33 and molecular heats 8 and 6. Sulphur dioxide, carbon disulphide, and some simple hydrocarbons give a mean ratio 1·25 and molecular heats 10 and 8, whilst still heavier molecules are found to give even lower ratios and higher molecular heats.

Special interest attaches to the case of mercury, which appears with helium and argon in a special class, giving a ratio which is much higher than the figure 1·4 characteristic of the diatomic gases, and agreeing closely with the theoretical value 1·67. In the case of so heavy a molecule as mercury, this can only mean that the number of atoms is less than two. The molecule must therefore be monatomic, a conclusion that is in agreement with the rather scanty data for the vapour-density of mercury and its compounds.

These observations supply a remarkable proof of the correctness of Avogadro's fundamental proposition, that the molecules of the elements nitrogen and oxygen are of the same complexity as those of the compound nitric oxide, that hydrogen and chlorine are as complex as hydrogen chloride, and so forth.

Determination of Exact Molecular Weights by Means of Avogadro's Hypothesis.

(*a*) Avogadro's hypothesis implies that *the density of a gas or vapour at a given temperature and pressure is proportional to the weight of its molecules.* Thus, if the weights of 1 litre of oxygen and hydrogen at 0° and 760 mm. are 1·42900 and 0·089873 grams respectively, and there are *n* molecules in 1 litre of either gas, then—

$$\frac{1\cdot42900 \text{ grams}}{0\cdot089873 \text{ gram}} = \frac{\text{Weight of 1 litre of oxygen}}{\text{Weight of 1 litre of hydrogen}}$$
$$= \frac{\text{Weight of } n \text{ molecules of oxygen}}{\text{Weight of } n \text{ molecules of hydrogen}}$$
$$= \frac{\text{Weight of 1 molecule of oxygen}}{\text{Weight of 1 molecule of hydrogen}}.$$

For the purposes of the argument it is not necessary to know the actual number of molecules in the litre of gas, but recent experiments have shown that the number *n* has the value $2{\cdot}705 \times 10^{22}$, the error in this number being estimated at about 1 part in 1000. The AVOGADRO CONSTANT, *N*, which represents the number of atoms in the gram-atom or of molecules in the gram-molecule, *e.g.*, oxygen atoms in 16 grams of oxygen, or oxygen molecules in 32 grams of oxygen, is $60{\cdot}62 \times 10^{22}$.

(*b*) With the help of Avogadro's hypothesis it should be possible by making exact measurements of density to secure exact determinations of the molecular weights of gases. Modern work has shown, however, that Avogadro's hypothesis, like Gay-Lussac's law of volumes, is not an exact law, except perhaps at very low pressures. It can therefore only be used to calculate exact molecular weights after correcting

the observed densities for the slightly unequal compressibilities of different gases in the range from zero to atmospheric pressure (p. 129). The effect of these corrections is shown in the following table :—

TABLE 15.—RELATIVE DENSITIES AND EXACT MOLECULAR WEIGHTS OF GASES.

Gas.	Formula.	Relative densities compared with O_2=32. (a) At one atmosphere.	(b) Reduced to zero pressure.	Mol. wts. deduced from equivalents.
Hydrogen . . .	H_2	2·0125	2·0150	2·0152
Nitrogen . . .	N_2	28·007	28·013	28·02
Carbonic oxide . .	CO	28·001	28·003	28·005
Oxygen . . .	O_2	32	32	32
Carbonic anhydride .	CO_2	44·267	44·003	44·005
Nitrous oxide . .	N_2O	44·284	44·000	44·02
Hydrogen chloride .	HCl	36·741	36·484	36·457
Sulphurous anhydride .	SO_2	65·536	64·065	64·06

From these molecular weights the atomic weights of the different elements can be deduced as follows :

TABLE 16.—ATOMIC WEIGHTS DEDUCED BY AVOGADRO'S HYPOTHESIS.

Element.		Atomic weights deduced from densities.			Atomic weights deduced from equivalents.
Oxygen	=	16 (standard)			
Hydrogen	=	$\frac{2·0150}{2}$	=	1·0075	1·0076
Nitrogen	=	$\frac{28·013}{2}$	=	14·0065	14·008
	or	$\frac{44·000 - 16}{2}$	=	14·000	
Carbon	=	28·003 — 16	=	12·003	12·005
	or	44·003 — 32	=	12·003	
Chlorine	=	36·484 — 1·008	=	35·476	35·46
Sulphur	=	64·065 — 32	=	32·065	32·06

In each case the atomic weights deduced from the densities and from the equivalents agree very closely together.

SUMMARY AND SUPPLEMENT.

1. Avogadro's hypothesis states that

"*When the temperatures and pressures are the same, equal volumes of different gases contain equal numbers of molecules.*"

It is therefore possible to substitute molecules for volumes in any equation in which gases are involved. Thus, since

nitrogen	+	oxygen	=	nitric oxide
1 *vol.*		1 *vol.*		2 *vols.*

the molecules of gaseous nitrogen and of gaseous oxygen are divided into two parts in forming nitric oxide. The equation is therefore written

N_2	+	O_2	=	2NO
1 *vol.*		1 *vol.*		2 *vols.*

2. By determining the subdivision of the molecules of gaseous elements, it is possible to deduce not only the formulæ of gaseous elements, but also their *atomic weights*, the *formulæ* of their compounds and correct *equations* expressing chemical changes in gases. The correctness of the formulæ thus deduced is confirmed when the gases are grouped according to the magnitude of their molecular heats.

3. Avogadro's hypothesis is an approximation which becomes exact only at very low pressures. Densities observed at atmospheric pressures may be corrected by dividing them by the factor

$$1 + \lambda = (1 + a)(1 - b)$$

where a and b are the constants of Van der Waals's equation (p. 128) and λ (p. 129) is a constant which sums up the effects produced by a and b. Molecular and atomic weights determined by this method agree closely with those determined by analysis.

4. The actual number of molecules in a litre of gas at 0° and 760 mm. pressure is $2{\cdot}705 \times 10^{22}$, and in a gram-molecule of gas $60{\cdot}62 \times 10^{22}$.

CHAPTER XIV

APPLICATION OF AVOGADRO'S HYPOTHESIS TO CARBON COMPOUNDS

Extension of Avogadro's Hypothesis to Non-volatile Elements.

Avogadro's method of applying his hypothesis gives definite results as to atomic weights, formulæ, and equations when gaseous or readily-volatile elements and compounds are alone involved; but it breaks down as soon as non-volatile elements and compounds come into consideration. Thus, even in the case of sulphur and of phosphorus, it is not easy to carry out chemical changes in such a way as to measure the volumes of sulphur-vapour or of phosphorus-vapour that are concerned in the change; and in the case of carbon it is quite impossible to say what fraction of a molecule takes part in the formation of any of its compounds, since carbon vaporises only above 3000°, and we are therefore unable to determine the volume of carbon-vapour used up or liberated in any chemical change. In the following paragraphs an account is given of the methods used in applying Avogadro's hypothesis to these more difficult cases.

Cannizzaro's Method of determining Atomic Weights.

A method of applying Avogadro's hypothesis in such a way as to include elements which cannot themselves be vaporised, although they form volatile compounds, was developed by Cannizzaro in 1858. This method depends on tabulating the *vapour density* and the *percentage composition* as determined experimentally for a large number of volatile compounds of each element. From the vapour density the *molecular weight* is calculated with the help of Avogadro's hypothesis, and from the percentage composition the *molecular composition* can then be determined, *i.e.*, the weight of each element that is contained in the molecular weight of the compound. *The smallest weight of an element that is found in the molecular weight of any of its compounds is taken as the atomic weight of the element.* The argument may be expressed as follows: Avogadro's hypothesis states that for any volatile substance

$$\frac{\textit{Density of vapour}}{\textit{Density of hydrogen}} = \frac{\textit{molecular weight of vapour}}{\textit{molecular weight of hydrogen}}.$$

If the density of hydrogen be taken as unity and its molecular weight be taken as 2, it follows that

$$\frac{\textit{Density of vapour}}{1} = \frac{\textit{molecular weight of vapour}}{2},$$

or that *the molecular weight of the vapour relatively to the hydrogen atom is twice its vapour density relatively to hydrogen gas.* The data, worked out on this basis for hydrogen, oxygen, carbon, and chlorine, are given in Table 17 (pp. 146–147).

(i) In compiling this table, RELATIVE DENSITIES instead of ABSOLUTE DENSITIES, *e.g.*, in grams per litre, have been taken in column *2* for the various gases and vapours, since *the relative densities are almost independent of temperature and pressure,* and can therefore be determined at any temperature or pressure that may be required for the convenient vaporisation of the substance. Thus, it would be of little value to compare the vapour-density of steam at 100° with the density of hydrogen or of oxygen at 0° ; but a useful comparison may be made of the density of steam with that of a standard gas at 100°, and of the densities of hydrogen and oxygen with that of the same standard gas at 0°, and these relative densities may then be compared directly with one another. At one time air was commonly chosen as the standard, but hydrogen was preferred by Cannizzaro because it is the lightest of the gases, and therefore gives numbers greater than unity for the relative densities of all other gases and vapours.

(ii) Assuming the hydrogen molecule to be diatomic, we have

$$H = 1, \quad H_2 = 2,$$

and the vapour density of each substance relative to hydrogen (column *2*) is converted into a molecular weight (column *7*) by multiplying it by 2, this being the molecular weight of hydrogen. Thus in the case of alcohol we have

Vapour density	=	23
Molecular weight	=	23 × 2 = 46.

The assumption that the molecules of hydrogen gas are diatomic is justified by the fact that in the subsequent portions of the table the atomic weight of hydrogen is worked out as H = 1, and no further subdivision of the molecule can be detected.

At the present time atomic and molecular weights are always calculated relatively to

$$O = 16, \quad O_2 = 32$$

when $H = 1{\cdot}008, \quad H_2 = 2{\cdot}016.$

The difference between these two standards, amounting to less than 1 per cent., is not important in the present instance in view of the low degree of accuracy reached in ordinary determinations of vapour density, and of the fact that Avogadro's hypothesis as usually applied is only an approximation.

TABLE 17.—ATOMIC WEIGHTS,

EXPERIMENTAL.

Column No. *1*	Vapour density. *2*	Percentage composition. *3* H	*4* O	*5* C	*6* Cl
Hydrogen	1	100	—	—	—
Oxygen	16	—	100	—	—
Ozone	24	—	100	—	—
Chlorine	35½	—	—	—	100
Steam	9	11·1	88·9	—	—
Hydrogen chloride	18¼	2·7	—	—	97·3
Carbonic oxide	14	—	57·2	42·8	—
Carbonic anhydride	22	—	72·7	27·3	—
Marsh gas	8	25	—	75	—
Olefiant gas	14	14·3	—	85·7	—
Acetylene	13	7·7	—	92·3	—
Benzene	39	7·7	—	92·3	—
Turpentine	68	11·8	—	88·2	—
Alcohol	23	13·0	34·8	52·2	—
Ether	37	13·5	21·6	64·9	—
Ethyl chloride	32¼	7·7	—	37·2	55·1
Ethylene chloride	49½	4·0	—	24·3	71·7
Chloroform	59¾	0·8	—	10·0	89·2
Carbon tetrachloride	77	—		7·8	92·2

(iii) By multiplying the percentage composition (columns *3* to *6*) into the molecular weight (column *7*) the molecular composition is determined as set out in columns *8* to *11*, *e.g.*, in the case of alcohol 13% of 46 = 6; 34·8% of 46 = 16; 52·2% of 46 = 24.

(iv) The highest common factor in each of the columns *8* to *11* is taken as the atomic weight of the element concerned, namely,

$$H = 1, \quad O = 16, \quad C = 12, \quad Cl = 35\tfrac{1}{2}.$$

Although the element carbon cannot be included in this table, since its vapour density and molecular weight are still unknown, it is quite clear that the atomic weight of carbon is 12, since this is the highest common factor of all the numbers in the "carbon" column.

(v) By dividing these atomic weights into the molecular compositions (columns *8* to *11*), the number of atoms of each element in the molecule (columns *12*–*15*), and therefore the formula of the compound (column *16*), can be deduced, *e.g.*, in the case of alcohol

6 parts of hydrogen $= 1 \times 6 = H_6$
16 ,, oxygen $= 16 \times 1 = O_1$
24 ,, carbon $= 12 \times 2 = C_2$

and the formula is $H_6O_1C_2$, or, as it is more commonly written, C_2H_6O.

MOLECULAR WEIGHTS, AND FORMULÆ.

THEORETICAL.

Molecular weight.	Molecular composition.				Atoms of				Formula.
7	8	9	10	11	12	13	14	15	16
	H	O	C	Cl	H	O	C	Cl	
2	2	—	—	—	2	—	—	—	H_2
32	—	32	—	—	—	2	—	—	O_2
48	—	48	—	—	—	3	—	—	O_3
71	—	—	—	71	—	—	—	2	Cl_2
18	2	16	—	—	2	1	—	—	H_2O
36½	1	—	—	35½	1	—	—	1	HCl
28	—	16	12	—	—	1	1	—	CO
44	—	32	12	—	—	2	1	—	CO_2
16	4	—	12	—	4	—	1	—	CH_4
28	4	—	24	—	4	—	2	—	C_2H_4
26	2	—	24	—	2	—	2	—	C_2H_2
78	6	—	72	—	6	—	6	—	C_6H_6
136	16	—	120	—	16	—	10	—	$C_{10}H_{16}$
46	6	16	24	—	6	1	2	—	C_2H_6O
74	10	16	48	—	10	1	4	—	$C_4H_{10}O$
64½	5	—	24	35½	5	—	2	1	C_2H_5Cl
99	4	—	24	71	4	—	2	2	$C_2H_4Cl_2$
119½	1	—	12	106½	1	—	1	3	$CHCl_3$
154	—	—	12	142	—	—	1	4	CCl_4
H.C.F. =	1	16	12	35½					

Atomic Weights	H	=	1	O	=	16
	C	=	12	Cl	=	35½

(vi) By means of precisely similar tables it can be shown that

N = 14, S = 32, Br = 80, I = 127, etc.

Molecular Formulæ of Volatile Compounds.

When the atomic weights of its elements are known, the molecular formula of any volatile compound may be deduced from its vapour density and percentage composition as follows :—

Phosphorus oxychloride.

Vapour density = 76·75 ; hence molecular weight = 153·5.

The percentage composition is

P = 20·2% ; O = 10·4% ; Cl = 69·4%

Therefore the composition of a molecule weighing 153·5 is

P = 30·99 ; O = 15·97 ; Cl = 106·5.

Since the atomic weights are

P = 31, O = 16, Cl = 35·5,

the formula of phosphorus oxychloride is $POCl_3$.

Nitrobenzene.

Vapour density = 61·5; hence molecular weight = 123.

The percentage composition is

$$C = 58{\cdot}5\%;\quad H = 4{\cdot}1\%;\quad O = 26{\cdot}0\%;\quad N = 11{\cdot}4\%.$$

Therefore in a molecule weighing 123 we have

$$C = 71{\cdot}9;\quad H = 5{\cdot}05;\quad O = 32;\quad N = 14;$$

or

$$C = 6 \times 12;\ H = 5 \times 1;\ O = 2 \times 16;\ N = 1 \times 14,$$

and the formulæ of nitrobenzene is $C_6H_5O_2N$.

Empirical and Molecular Formulæ.

In the case of volatile compounds it is possible from the vapour density and the percentage composition to calculate a MOLECULAR FORMULA, which shows the number as well as the nature of the different atoms which make up the molecule. In the case of non-volatile compounds, where the molecular weight cannot be determined, the atomic weights deduced from Avogadro's hypothesis can still be used to express the composition of the compound by means of an EMPIRICAL FORMULA, which shows the nature and the relative proportions of the atoms of each element, but not the actual number present in the molecule, since the weight of this is not known.

The method adopted in determining the empirical formula of a compound is as follows :—

(i) Divide the percentage of each element by its atomic weight, *e.g., in the case of nitrobenzene we have*

	C		H		O		N
Percentage composition	58·5	:	4·1	:	26·0	:	11·4 per cent.
Atomic weights	12		1		16		14
Ratios	$\frac{58{\cdot}5}{12}$	:	$\frac{4{\cdot}1}{1}$	:	$\frac{26{\cdot}0}{16}$	:	$\frac{11{\cdot}4}{14}$
	or 4·875	:	4·1	:	1·625	:	0·814

(ii) Divide the smallest of these ratios into the others

6·0 : 5·0 : 2·0 : 1

These quotients are the relative numbers of atoms of each element in the formula of the compound, which is therefore

$$C_6H_5O_2N$$

(iii) If fractions are present at this stage of the calculation they are converted into integers by multiplying the whole formula by a suitable factor, *e.g.*, $C_2H_3O1{\cdot}5$ would be written $C_4H_6O_3$.

Empirical formulæ are used in all cases in which the molecular weight of a compound is unknown, and even when the molecular weight

can be determined it is usual first to calculate an empirical formula to express the percentage composition of the compound, and then to determine by what factor it must be multiplied to give a molecular formula corresponding with the molecular weight of the compound.

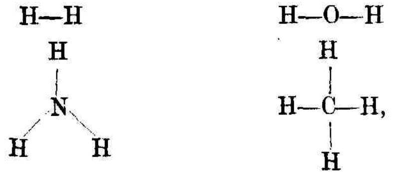
The molecular formula may be identical with the empirical formula or a multiple of it. For instance, formaldehyde, acetic acid, and grape-sugar have all the same composition and therefore the same empirical formula CH_2O, but the molecular formula of formaldehyde is identical with the empirical formula CH_2O, whilst the molecular formula of acetic acid is $(CH_2O)_2$, or $C_2H_4O_2$, and the molecular formula of grape-sugar is $(CH_2O)_6$ or $C_6H_{12}O_6$. Again, acetylene and benzene are both represented by the empirical formula CH, but the molecular formula of acetylene is $(CH)_2$ or C_2H_2, and that of benzene is $(CH)_6$ or C_6H_6.

Valency of Non-metals. Graphical and Structural Formulæ.

When the formulæ of non-metallic hydrides are examined it is seen that they can be classified as follows :—

Univalent hydrides, e.g.,	HCl, HBr,HI, and HH (hydrogen gas).
Bivalent hydrides, e.g.,	OH_2, SH_2.
Tervalent hydrides, e.g.,	NH_3, PH_3.
Quadrivalent hydrides, e.g.,	CH_4, SiH_4.

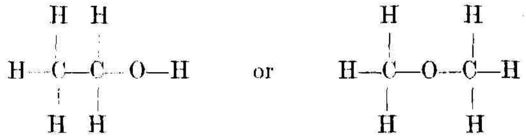
In the univalent hydrides the equivalent, which combines with 1·008 grams of hydrogen, is identical with the atomic weight of the element; in the bivalent hydrides it is half the atomic weight; in the tervalent hydrides it is one-third and in the quadrivalent hydrides one-fourth of the atomic weight. The valency of these elements may therefore be defined as the *number of hydrogen atoms with which one atom of the element will combine.* From this point of view the valency may be regarded as a measure of the combining power of the element. Each unit of valency is regarded as a BOND by which an atom of hydrogen or of some other element may be united to the element in question as shown in the formulæ



in which hydrogen is represented as possessing only one bond, and therefore not capable of joining together other atoms, whilst oxygen, nitrogen, and carbon with 2, 3, and 4 bonds may serve as a nucleus in building up comparatively complex molecules.

The study of GRAPHICAL FORMULÆ, in which the important bonds are shown pictorially, and of STRUCTURAL FORMULÆ, in which the

arrangement of the atoms in the molecule is shown without necessarily showing all the individual bonds, is of special importance in connection with carbon compounds. Thus, assuming the valencies of hydrogen, oxygen, and carbon to be 1, 2, and 4 respectively, the molecule of alcohol, C_2H_6O, may either contain the chain C—C—O, or the chain C—O—C. In either case the remaining valencies of these atoms will provide for the linking on of 6 univalent atoms, as is seen in the GRAPHICAL FORMULÆ,



In the first of these formulæ the 6 hydrogen atoms appear in groups of 3, 2, and 1 respectively, whilst in the second formula there are two precisely similar groups of 3 + 3 hydrogen atoms. This is shown equally clearly when the abbreviated STRUCTURAL FORMULÆ are used thus:

$$CH_3{\cdot}CH_2{\cdot}OH \quad \text{and} \quad CH_3{\cdot}O{\cdot}CH_3$$

where the dots represent bonds uniting together the univalent radicals CH_3— and —OH, and the bivalent radicals —CH_2— and —O—.

The first formula is shown to be correct by the fact that sodium replaces only *one* atom of hydrogen in alcohol,

$$\underset{\text{Alcohol}}{2C_2H_6O} + 2Na = \underset{\text{Sodium ethoxide}}{2C_2H_5ONa} + H_2,$$

whilst hydrogen chloride replaces both hydrogen and oxygen by chlorine, exactly as in the neutralisation of caustic soda,

$$\underset{\text{Alcohol}}{C_2H_5{\cdot}OH} + HCl = \underset{\text{Ethyl chloride}}{C_2H_5Cl} + H_2O;$$

compare $\quad NaOH + HCl = NaCl + H_2O.$

The COMPOUND RADICAL, or group of atoms, C_2H_5, which takes the place of sodium in the second of these actions, is called ETHYL and is sometimes represented by the symbol Et. Alcohol itself is described as **ethyl alcohol** or **ethyl hydroxide,** and may be written as $C_2H_5{\cdot}OH$ or EtOH. The solid product of the first action is called **sodium ethoxide,** $NaOC_2H_5$ or NaOEt; compare sodium hydroxide, NaOH. The product of the second action, **ethyl chloride,** C_2H_5Cl or EtCl, is a very volatile liquid, which has the formula of a salt but the properties of an ether; *it is therefore classed as an* ETHEREAL SALT, *or more shortly as an* ESTER.

A fuller proof of the correctness of the formula $CH_3{\cdot}CH_2{\cdot}OH$ for alcohol is found in the fact that by the successive action of oxygen, chlorine, and caustic soda it can be converted into a compound, **sodium trichloroacetate,** $C_2Cl_3O_2Na$, in which 1 hydrogen atom has

been replaced by sodium (1 atom), 2 atoms by oxygen (1 atom), and 3 atoms by chlorine (3 atoms), as shown in the structural formulæ

$$CH_3{\cdot}CH_2{\cdot}OH \longrightarrow CCl_3{\cdot}CO{\cdot}ONa.$$

SUMMARY AND SUPPLEMENT.

1. **Avogadro's hypothesis** may be extended to *non-volatile elements* such as carbon, by tabulating the vapour density and composition of their volatile compounds, and deducing from these numbers the molecular weight and *molecular composition of the compounds.*

The smallest weight of an element that is found in the molecular weight of any of its compounds is taken as the atomic weight of the element.

2. By this process **molecular formulæ** of volatile compounds can be determined even when they contain non-volatile elements such as carbon. In the case of non-volatile compounds an **empirical formula** can be deduced, which shows the relative proportions of the atoms of each element, but not their actual numbers in the molecule.

3. The **valency of a non-metal,** *i.e.*, the ratio of its atomic weight to its equivalent, is identical with the number of hydrogen atoms with which one atom of the element will combine; it may therefore be regarded as a measure *of the combining power of the element.* By studying the valencies it is possible to determine the way in which the atoms are linked together in a molecule and to express this by means of a **graphical** or a **structural formula.**

CHAPTER XV

EXTENSION OF AVOGADRO'S HYPOTHESIS TO METALLIC COMPOUNDS

Equivalents of the Metals.

Full details have already been given in Chapters VII, VIII, and IX of the experimental work by which the combining-weights of the non-metals hydrogen, oxygen, and carbon were determined. In the case of the metals, the equivalents are usually determined either by direct combination of the metal with oxygen, or much more frequently by analysing the compounds of the metal with chlorine. The chlorides are often better for this purpose than the oxides, not only because they are more readily prepared in a pure state, but also because in the case of all but the lightest metals, the ratio of the elements is smaller, *e.g.*,

$$\begin{cases} \textit{Cadmium} : \textit{oxygen} = 112 : 16 \\ \textit{Cadmium} : \textit{chlorine} = 112 : 71 \end{cases}$$

$$\begin{cases} \textit{Lead} : \textit{oxygen} = 207 : 16 \\ \textit{Lead} : \textit{chlorine} = 207 : 71 \end{cases}$$

Bromides, which resemble the chlorides, but are of higher molecular weight, are sometimes used instead of chlorides in these analyses, since they are often less soluble and therefore more easily purified, and, in the case of elements of high atomic weight, give a more evenly balanced composition than the chlorides, *e.g.*,

$$\begin{cases} \textit{Radium} : \textit{chlorine} = 226 : 71 \\ \textit{Radium} : \textit{bromine} = 226 : 160 \end{cases}$$

During the twenty-five years from 1857 to 1882, Stas determined with very great care the combining-weights of the ten elements

nitrogen, sulphur, chlorine, bromine, iodine,
lithium, sodium, potassium, silver, lead,

relatively to oxygen. For this purpose he made very careful analyses of a series of oxygen salts, *e.g.*, of potassium chlorate, which served to give the combining-weights of the non-metal chlorine and of the metals potassium and silver relatively to oxygen.

(*a*) Potassium chlorate, which contains six equivalents of oxygen in combination with one of potassium and one of chlorine, was converted into potassium chloride by removing the oxygen

(i) by ignition,

(ii) by heating with hydrochloric acid.

It was found that 100 parts of potassium chlorate gave 60·846 parts of potassium chloride and therefore lost in this process 39·154 parts of oxygen; six equivalents, or 48 parts, of oxygen were therefore combined with $48 \times \frac{60 \cdot 846}{39 \cdot 154} = \mathbf{74 \cdot 592}$ parts of potassium chloride. This number is the equivalent of *potassium chloride*.

(*b*) The weight of potassium chloride was determined which was required to precipitate (as silver chloride) a known weight of silver dissolved in nitric acid. It was found that 74·592 parts of potassium chloride would precipitate **107·943** parts of silver; this number is the equivalent of *silver*.

(*c*) By a variety of methods it was found that 100 parts of silver combined with 32·845 parts of chlorine to form 132·845 parts of silver chloride. Since in these experiments 107·943 parts of silver combined with $\frac{32 \cdot 845}{100} \times 107 \cdot 943 = \mathbf{35 \cdot 454}$ parts of chlorine, this number is the equivalent of *chlorine*.

(*d*) Subtracting 35·454 (the equivalent of chlorine) from 74·592 (the equivalent of potassium chloride), the equivalent of *potassium* is found to be **39·138**.

The analysis of potassium chlorate has the advantage that the three elements are present in comparable quantities, the proportions being approximately

$$\textit{potassium} : \textit{chlorine} : \textit{oxygen} = 39 : 35\tfrac{1}{2} : 48 \, ;$$

in this way the difficulties are avoided which arise from the somewhat extreme ratio of hydrogen to oxygen in water, and the still more extreme ratio of hydrogen to chlorine in hydrogen chloride. Similar determinations of the ratios of silver to silver sulphide and of silver to silver sulphate gave the ratios *silver* : *sulphur* : *oxygen* in silver sulphate and hence the equivalents of *silver* and *sulphur*.

The equivalent of the "nitrate" radical was determined by converting the chlorides of lithium, sodium, and potassium into nitrates by evaporation with nitric acid. Taking the equivalent of chlorine as 35·4529, the equivalent of the "nitrate" radical was found to be **62·0438**, containing 48 parts of oxygen and therefore **14·0438** parts of *nitrogen*.

Analysis of Chlorides.

An important factor in these determinations is the insolubility of silver chloride, which makes it exceptionally easy to secure complete precipitation in the form of silver chloride, either of *silver* from its soluble salts by the addition of a soluble chloride, or of *chlorine* from a soluble chloride by the addition of silver nitrate. Two general methods may be used for determining the composition of a metallic chloride.

(*a*) *Gravimetric Method.*—A weighed quantity of the chloride is dissolved in water and an excess of silver nitrate solution added. The whole of the chlorine is thus precipitated as silver chloride, in which

form it can be collected, washed, dried, melted to remove the last traces of water, and weighed. The percentage of silver and therefore of chlorine in silver chloride can be determined by precisely similar experiments in which a known weight of pure silver is dissolved in nitric acid and precipitated as silver chloride, by the addition to the solution of a soluble chloride.

In modern practice a precipitate of silver chloride is usually collected in a GOOCH CRUCIBLE, Fig. 58, the bottom of which is perforated with a series of tiny holes, on which a filter of asbestos is formed by pouring into the crucible minute fibres of asbestos suspended in water. A filter-pump (p. 17) is used to drain the liquid through the crucible. This method of working has the advantage that the precipitate can be dried to constant weight, and if necessary ignited, without change of weight either of the crucible or of the asbestos filter, provided that these have been treated in a similar manner before collecting the precipitate. The clotting of the silver chloride precipitate when stirred or boiled is an important factor in facilitating filtration.

(*b*) *Volumetric Method.*—The quantity of silver required to precipitate the chlorine in a metallic chloride may be determined exactly by dissolving pure silver in nitric acid, evaporating to dryness to remove excess of acid, redissolving the silver nitrate in water, and diluting to a known volume or weight of standard solution. The chloride to be analysed is weighed out and dissolved in water; the standard solution of silver nitrate is then added in such a quantity as to precipitate almost the whole of the chlorine in the form of silver chloride. The solution is then heated or shaken until the precipitate of silver chloride has clotted and left a clear solution above it. Smaller quantities of silver nitrate are then added until they no longer cause any fresh cloudiness in the solution. In this way it is possible to determine with very great accuracy the amount of silver that is required to unite with the chlorine in the compound under examination, and hence the amount of chlorine which it contains, since the ratio of silver to chlorine is already known very accurately from the gravimetric synthesis of silver chloride.

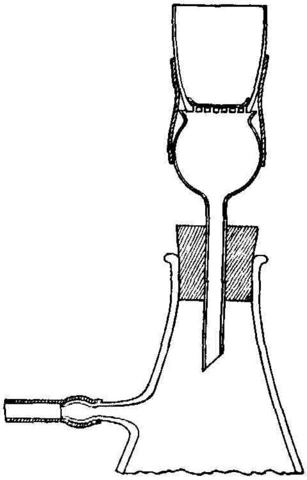


FIG. 58.—GOOCH CRUCIBLE ARRANGED FOR FILTRATION.

Atomic Weights of the Metals.

Even when their equivalents have been determined accurately, the atomic weights of the metals cannot be deduced directly by means

of Avogadro's hypothesis, since the number of volatile metallic compounds is much too small. Thus in the case of iron the experimental values for the vapour-densities of its volatile compounds relatively to hydrogen, when multiplied by two in order to convert them into molecular weights, are as follows :—

Compound.	*Molecular weight.*	*Weight of iron in molecular weight.*
Ferrous chloride . .	125·6	56 (about)
Ferric chloride . .	332·2	112 ,,
Iron carbonyl . .	199·0	56 ,,

The last column shows the weight of iron in the molecular weight, rounded off to the nearest multiple of the equivalent of iron. The highest common factor of the numbers in this column is 56, but it would be impossible to conclude from so short a table that the atomic weight of iron might not be some smaller fraction of this number, such as 28 or 18·7 or 14. In practice, therefore, the atomic weights of the metals must be determined by indirect applications of Avogadro's hypothesis as follows.

Atomic Heats of Solid Elements.

Dulong and Petit in 1819 discovered that a constant product was obtained when the specific heats of a number of solid elements were multiplied by values for their atomic weights deduced either directly by means of Avogadro's hypothesis or from analogies with elements of known atomic weight. Dulong and Petit's LAW OF ATOMIC HEATS states that

the atomic heat of the solid elements is constant

or alternatively that

the atoms of all solid elements have the same capacity for heat.

It may be expressed algebraically in the form

$$\textit{specific heat} \times \textit{atomic weight} = \textit{atomic heat} = 6{\cdot}3.$$

The product of the specific heat and atomic weight, which is called the ATOMIC HEAT of the element, has an average value of 6 in the range of temperatures from $+20^\circ$ to $+100^\circ$, falling to 5 in the range from $+20^\circ$ to -188°. These averages are, however, reduced by the inclusion of a few non-metals which have exceptionally small atomic heats. When the metals alone are considered, the average value of the atomic heats is about 6·3 in the range from 20° to 100°.

When the specific heat of a metal is known, an approximate value for the atomic weight may be calculated by means of Dulong and Petit's law. This value will be even less exact than the value deduced for a non-metal by a direct application of Avogadro's hypothesis, but

it will usually suffice to indicate the valency of the metal. Thus, in the case of a few typical metals we have the following figures :—

TABLE 18.—SPECIFIC AND ATOMIC HEATS OF THE METALS.

Element.	*Equivalent.*	*Sp. ht.* (20 to 100°).	*Approx. atomic weight.*	*Valency.*	*Exact at. wt.* (*Equiv.* × *valency.*)	*At. ht.* (*At. wt.* × *sp. heat.*)
1	*2*	*3*	*4*	*5*	*6*	*7*
Iron .	27·92	0·1146	About 55	2	55·84	6·4
Tin .	59·5	0·0556	About 113	2	119·0	6·6
Lead .	103·55	0·031	About 203	2	207·10	6·4
Copper	31·785	0·0936	About 67	2	63·57	6·0
Silver .	107·88	0·0566	About 111	1	107·88	6·1
Gold .	65·73	0·0316	About 199	3	197·2	6·2
					Mean	6·3

In this table the "approximate atomic weights" of column *4* are obtained by dividing the specific heats of column *3* into a fixed number 6·3 representing the average atomic heat of the metals. A comparison of columns *2* and *4* gives the integral valencies of column *5*. The exact atomic weights of column *6* are then obtained by multiplying together the equivalent (column *2*) and the valency (column *5*). In column *7* the individual values for the atomic heat (specific heat × exact atomic weight) are given in order to show the variations from the average value 6·3 of this "constant."

Abnormal Atomic Heats.

Several elements of small atomic weight give exceptionally low values for the atomic heat. These abnormalities become exaggerated when the temperature is lowered, but tend to disappear when the temperature is raised. Thus, the atomic heat of carbon in the form of diamond falls from a mean value of 1·84 over the range from + 20 to + 100° to 0·03 at — 181°, but increases to 5·45 when the temperature is raised to + 900°. In the same way, the atomic heat of boron at + 26°, which is already very low at 2·62 as compared with the mean value of 6·3, falls to 0·24 at — 224° but rises to 4·03 at + 233°. At very low temperatures, Dulong and Petit's law becomes altogether invalid (see below, p. 547), but at atmospheric temperatures the only important exceptions are found in the case of a few non-metals of small atomic weight, to which Avogadro's hypothesis can be applied directly, since they form large numbers of volatile compounds. These exceptions do not therefore interfere with the practical application of the law as an important means of determining the atomic weights of metals which do not form volatile compounds.

Molecular Heats of Solid Compounds.

In a large number of cases the solid elements retain their capacity for heat unaltered when combined to form solid compounds. In these

compounds then the MOLECULAR HEAT (*i.e.*, specific heat × molecular weight) is equal to the number of atoms multiplied by 6·3.

The following figures were quoted by Cannizzaro as evidence that the atomic weight of mercury is 200, and not 100 as had been supposed previously.

TABLE 19.—ATOMIC AND MOLECULAR HEATS OF SOLIDS.

Atomic heats :	
Solid bromine, Br*	80 × 0·0843 = 6·746
Iodine, I*	127 × 0·0541 = 6·873
Solid mercury, Hg	200 × 0·0324 = 6·482
Molecular heats :	
Mercurous chloride, HgCl*	(200 + 35·5) × 0·0521 = 12·258 = 2×6·129
Mercurous iodide, HgI*	(200 + 127) × 0·0395 = 12·913 = 2×6·457
Mercuric chloride, $HgCl_2$	(200 + 71) × 0·0689 = 18·669 = 3×6·223
Mercuric iodide, HgI_2	(200 + 254) × 0·0420 = 19·054 = 3×6·351

* The argument is not affected by writing these formulæ as Br_2, I_2, Hg_2Cl_2, Hg_2I_2.

The Law of Isomorphism.

The atomic weights of the metals can also be determined by means of the LAW OF ISOMORPHISM, which states that

" *Substances which are similar in crystalline form and in chemical properties can usually be represented by similar formulæ.*"

Thus, the phosphates and arsenates represented by the following pairs of formulæ

NaH_2PO_4,H_2O	KH_2PO_4	$(NH_4)H_2PO_4$
NaH_2AsO_4,H_2O	KH_2AsO_4	$(NH_4)H_2AsO_4$

were shown by Mitscherlich in 1819 to be isomorphous, and one set of formulæ can be changed into the other merely by writing As instead of P. As 31 is the atomic weight of phosphorus, and 31 *parts of phosphorus* are replaced by 75 *parts of arsenic* on passing from one compound to the other, it follows that 75 must be the atomic weight of *arsenic.*

In the same way, in the isomorphous perchlorates and permanganates (*e.g.*, $KClO_4$ and $KMnO_4$), 35·5 *parts of chlorine* are replaced by 55 *parts of manganese*, and 55 is therefore the atomic weight of *manganese.* Again, in the isomorphous sulphates and chromates (*e.g.*, K_2SO_4 and K_2CrO_4), 32 *parts of sulphur* are replaced by 52 *parts of chromium,* and 52 is therefore the atomic weight of *chromium.*

These examples of isomorphism were used in order to bridge the gap between the non-metals chlorine and sulphur, of which the atomic weights can be determined directly from Avogadro's hypothesis, and the metals to which atomic weights cannot be assigned by this method. Thus, having once established suitable values for manganese and chromium, it is easy to deduce values for the atomic weights of other metals by making use of other isomorphous series, as in Table 20.

TABLE 20.—ISOMORPHOUS COMPOUNDS OF THE METALS.

(a) *The Alums.*	(b) *The Spinels.*	In (a) and (b).
$KCr(SO_4)_2,12H_2O$ 52	$FeCr_2O_4$ 2 × 52	if Cr = 52
$KFe(SO_4)_2,12H_2O$ 56	$FeFe_2O_4$ 2 × 56	then Fe = 56
$KAl(SO_4)_2,12H_2O$ 27	$MgAl_2O_4$ 2 × 27	and Al = 27

(c) *The Double Sulphates.*		In (c)
$K_2SO_4,MnSO_4,6H_2O$ 55	if	Mn = 55
$K_2SO_4,FeSO_4,6H_2O$ 56	then	Fe = 56
$K_2SO_4,CuSO_4,6H_2O$ 63	and	Cu = 63
$K_2SO_4,ZnSO_4,6H_2O$ 65	and	Zn = 65
$K_2SO_4,MgSO_4,6H_2O$ 24	and	Mg = 24

The law of isomorphism is, however, not a very sure guide, as many cases are known in which isomorphous compounds have dissimilar formulæ. Thus the atomic weights of silver and lead are 108 and 207, although in their isomorphous sulphides 216 parts of silver replace 207 parts of lead.

Argentite	Ag_2S 2 × 108
Galena	PbS 207

The final test in fixing the atomic weights of the metals is therefore the Periodic Classification of the Elements (Chapter XXXI), in which each metal should fall into a suitable position as soon as its atomic weight has been determined correctly.

Empirical Formulæ of Metallic Salts.

When the atomic weights of the metals have been established by the methods set out above, the empirical formulæ of their salts may be determined in precisely the same way as in the case of non-metallic compounds (p. 148), although the molecular formulæ are usually unknown. Four examples may be given :

(a) *Potassium Chlorate*.—This salt has the composition

Potassium.	*Chlorine.*	*Oxygen.*
K = 31·92%	Cl = 28·92%	O = 39·16%

The atomic weights are

K = 39·10	Cl = 35·46	O = 16 exactly.

The atomic ratios are therefore

$$K = \frac{31·92}{39·10} \qquad Cl = \frac{28·92}{35·46} \qquad O = \frac{39·16}{16}$$

$$= 0·816 \qquad = 0·816 \qquad = 2·448$$

or 1 : 1 : 3

and the formula is therefore $\mathbf{KClO_3}$.

(*b*) *Lead Nitrate.*—Berzelius found that 100 grams of this salt left, when ignited, 67·22 grams of litharge containing 62·37 grams of lead and 4·85 grams of oxygen; the acid radical consisted of 32·78 grams of nitric anhydride, containing nitrogen 8·52, oxygen 24·26. The percentage composition of the salt is therefore

	Lead.	*Nitrogen.*	*Oxygen.*
	Pb = 62·37%	N = 8·52%	O = 29·11%
The atomic weights are			
	Pb = 207·2	N = 14·01	O = 16 exactly.
The atomic ratios are therefore			
	$Pb = \frac{62 \cdot 37}{207 \cdot 2}$	$N = \frac{8 \cdot 52}{14 \cdot 01}$	$O = \frac{29 \cdot 11}{16}$
	= 0·301	= 0·608	= 1·820
or	1 :	2 :	6

and the formula is $\mathbf{PbN_2O_6}$.

(*c*) *Chalk.*—Berzelius found that 100 parts of chalk, when ignited, lost 43·6 parts of carbonic anhydride and left a residue of 56·4 parts of lime. The lime was analysed by converting it into its chloride and estimating the chlorine in the product as silver chloride, the difference representing metallic calcium derived from the lime. In this way he showed that the 56·4 parts of lime contained 39·9 parts of metallic calcium and 16·5 parts of oxygen, whilst the 43·6 parts of carbonic anhydride contained 12·4 parts of carbon and 31·2 parts of oxygen. The composition of chalk is therefore

	Calcium.	*Carbon.*	*Oxygen.*
	Ca = 39·9%	C = 12·4%	O = 47·7%
The atomic weights are			
	Ca = 40·1	C = 12·0	O = 16 exactly.
The atomic ratios are therefore			
	$Ca = \frac{39 \cdot 9}{40 \cdot 1}$	$C = \frac{12 \cdot 4}{12 \cdot 0}$	$O = \frac{47 \cdot 7}{16}$
	= 0·99	= 1·03	= 2·98
or	1 :	1 :	3

and the formula is $\mathbf{CaCO_3}$.

(*d*) *Schönite.*—The mineral schönite is found by analysis to contain

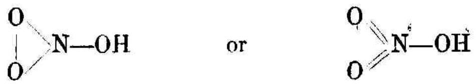
K	Mg	S	O	H_2O
K = 19·39%	Mg = 6·02%	S = 15·91%	O = 31·85%	H_2O = 26·85%
The atomic weights are				
K = 39·10	Mg = 24·32	S = 32·06	O = 16	H = 1·008
The atomic ratios are				H_2O = 18·016
$K = \frac{19 \cdot 39}{39 \cdot 10}$	$Mg = \frac{6 \cdot 02}{24 \cdot 32}$	$S = \frac{15 \cdot 91}{32 \cdot 06}$	$O = \frac{31 \cdot 85}{16}$	$H_2O = \frac{26 \cdot 85}{18 \cdot 016}$
= 0·496	= 0·248	= 0·496	= 1·990	= 1·490
or 2 :	1 :	2 :	8 :	6

and the formula is $\mathbf{K_2MgS_2O_8,6H_2O}$.

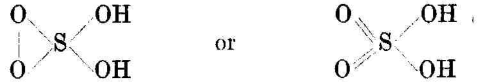
Structural Formulæ of Metallic Salts.

The determination of the structural formulæ of metallic salts is rendered difficult (*a*) by the fact that their molecular formulæ are usually unknown, (*b*) by the flexibility of the acids from which they are

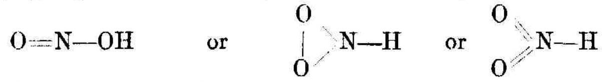
derived. Thus, whilst hydroxyl groups are certainly present in nitric and in sulphuric acids, which may be written as $NO_2{\cdot}OH$ and $SO_2(OH)_2$, it is uncertain how the bonds are arranged in the univalent NO'_2 and bivalent SO''_2 radicals * of these acids, *e.g.*, nitric acid may be



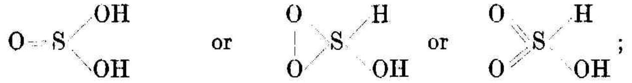
and sulphuric acid may be



In the case of nitrous and sulphurous acids, which contain one atom of oxygen less than nitric and sulphuric acids, even the presence of the hydroxyl groups is uncertain, *e.g.*, nitrous acid may be



and sulphurous acid may be



in each case related compounds have been prepared both with and without the doubtful hydroxyl group, but it is still uncertain to which type the acids and their salts belong.

Equations involving Empirical Formulæ.

When dealing only with gases, it is possible to express chemical changes by means of equations showing the molecular formulæ of all the substances concerned. In view of the fact that oxygen gas, O_2, and oxygen in the form of ozone, O_3, have totally different properties, and that atomic oxygen, represented by the formula O, would probably be far more active even than ozone, and perhaps as violent as fluorine in its action, it is usual to write out equations in such a form as to show *complete molecules of all gases of which the molecular formulæ are known*, *e.g.*, the combustion of gaseous hydrogen and oxygen is represented by the equation

$$2H_2 + O_2 = 2H_2O,$$

and not by the equation

$$H_2 + O = H_2O.$$

If in any case it is desired, in order to avoid complexity, to represent only a fraction of a molecule as taking part in an action, this may be shown legitimately by writing the equation in some such form as

$$H_2 + \tfrac{1}{2}O_2 = H_2O.$$

* The valency of the radical is shown by the dashes attached to the formula.

When liquids and solids are concerned, it is usual to assume that the molecules are not less complex than those of the vapour, and equations are therefore often adjusted so as to show cuprous chloride as Cu_2Cl_2 (corresponding with the density of its vapour), and not as CuCl, and mercurous chloride as Hg_2Cl_2, and not as HgCl. The general rule that an equation should not show a smaller quantity of a substance than that represented by the molecular formula of its vapour is not universally in force, since

(i) A misleading impression may be created by using the molecular formula of a vapour as if it were the molecular formula of the liquid or solid; *e.g.*, H_2O is certainly not the molecular formula of water, although it represents the composition of nearly all the molecules of steam.

(ii) In aqueous solutions, a profound dissociation of complex molecules may occur and give rise to simpler molecules than those of the vapour; soluble salts are therefore often represented by the simplest empirical formulæ, *e.g.*, ferric chloride is written as $FeCl_3$ and aluminium chloride as $AlCl_3$, although the vapours of these compounds contain the molecules Fe_2Cl_6 and Al_2Cl_6.

When dealing with solids, therefore, empirical formulæ are often used which would be definitely ruled out in the case of gases. Thus the combustion of sulphur is shown as

$$S + O_2 = SO_2, \text{ and not } S_8 + 8O_2 = 8SO_2,$$

although the molecule of sulphur probably has the formula S_8 at temperatures below about 500°; the combustion of phosphorus, on the other hand, is usually shown by the equation

$$P_4 + 5O_2 = P_4O_{10},$$

in view of the fact that molecular formulæ agreeing with the densities of the vapours can here be employed without making the equation unnecessarily complex. In the case of carbon, of which the molecular weight, both as vapour and solid, is entirely unknown, we usually write

$$C + O_2 = CO_2,$$

since we have no knowledge whatever as to the magnitude of the factor n in the molecular equation

$$C_n + nO_2 = nCO_2.$$

When dealing with equations in which metals are concerned, it is usual to represent all the reactions as those of single atoms of metal. This custom is justified by the fact that in almost every case in which the density of the metal has been determined in a gaseous state it has been found to be monoatomic. We therefore write

$$3Fe + 2O_2 = Fe_3O_4 \quad \text{and}$$
$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

Single atoms of hydrogen are also used sometimes in partial equations to represent actions in which mixtures capable of liberating hydrogen will bring about changes which cannot be effected by means of gaseous hydrogen. We therefore write

$$As + 3H = AsH_3$$

as being more correct than the equation

$$2As + 3H_2 = 2AsH_3,$$

which shows an action which cannot usually be effected by hydrogen gas.

In the same way, oxidation by means of oxidising agents may be shown by partial equations such as

$$2KI + H_2O + \dot{O} = I_2 + 2KOH,$$

where O represents oxygen produced in some simultaneous chemical change.

Valency of Metals and Formulæ of Metallic Salts.

Metallic salts are now commonly regarded as substances formed by displacing the hydrogen of an acid by a metal. The valency of the metal may then be defined as *the number of atoms of hydrogen which are displaced by each atom of the metal.* This definition is identical with the definition of valency as the ratio of the atomic weight to the equivalent of the metal. Thus, if the valency of a metal M be 1, 35·46 parts of chlorine will combine with one atomic proportion of the metal, and the formula of the chloride will be MCl, where the univalent metallic atom M displaces one atom of hydrogen in hydrogen chloride, HCl. If, however, the valency of the metal be 2, only half an atomic proportion of the metal will be combined with 35·46 parts of chlorine, and the formula of the chloride will be MCl_2, the bivalent metal displacing 2 atoms of hydrogen in 2HCl, and so on for metals of still higher valency.

(*a*) *Normal Salts.*—Typical formulæ of NORMAL SALTS, in which the whole of the hydrogen of the acid has been displaced by univalent sodium, Na′, bivalent magnesium, Mg″, tervalent aluminium, Al‴, or quadrivalent tin, Sn⁗, are shown in the following table

TABLE 21.—TYPICAL FORMULÆ OF METALLIC SALTS.

Acid.	*Sodium salt.*	*Magnesium salt.*	*Aluminium salt.*	*Stannic salt.*
Hydrochloric acid, HCl .	NaCl	$MgCl_2$	$AlCl_3$	$SnCl_4$
Nitric acid, HNO_3 . .	$NaNO_3$	$Mg(NO_3)_2$	$Al(NO_3)_3$	$Sn(NO_3)_4$
Sulphuric acid, H_2SO_4 .	Na_2SO_4	$MgSO_4$	$Al_2(SO_4)_3$	$Sn(SO_4)_2$
Carbonic acid, H_2CO_3 .	Na_2CO_3	$MgCO_3$	—	—
Phosphoric acid, H_3PO_4 .	Na_3PO_4	$Mg_3(PO_4)_2$	$AlPO_4$	

These normal salts are not necessarily neutral in their reaction, *e.g.*, sodium phosphate, Na_3PO_4, is strongly alkaline, and aluminium sulphate, $Al_2(SO_4)_3$, is acid.

(*b*) *Acid Salts.*—In the case of POLYBASIC ACIDS, *i.e.*, acids containing more than one atom of hydrogen displaceable by metals, the hydrogen may be displaced in stages, giving rise to ACID SALTS, *e.g.*, $NaHSO_4$ and NaH_2PO_4, thus:

Sulphuric acid, H_2SO_4, gives

(i) Sodium hydrogen sulphate (sodium bisulphate), $NaHSO_4$
(ii) Sodium sulphate, Na_2SO_4.

Phosphoric acid, H_3PO_4, gives
(i) Dihydrogen sodium phosphate (acid sodium phosphate), NaH_2PO_4
(ii) Disodium hydrogen phosphate (neutral sodium phosphate), Na_2HPO_4.
(iii) Trisodium phosphate (alkaline sodium phosphate), Na_3PO_4.

Acid salts may, however, be formed also from monobasic acids, especially when these show a tendency to polymerise, *e.g.*,

Hydrofluoric acid, HF, gives an acid potassium fluoride, KHF_2.
Nitric acid, HNO_3, gives acid nitrates such as $(NH_4)HN_2O_6$ or $(NH_4)NO_3,HNO_3$, and $(NH_4)H_2N_3O_9$ or $(NH_4)NO_3,2HNO_3$.

On the other hand, in some acids, only a part of the hydrogen is displaceable by metals, *e.g.*,

Persulphuric acid, H_2SO_5, is monobasic and gives a neutral sodium persulphate of the formula $NaHSO_5$.
Hypophosphorous acid, H_3PO_2, is monobasic and gives a neutral potassium hypophosphite, KH_2PO_2.
Acetic acid, $C_2H_4O_2$, is monobasic and only gives a sodium salt of the formula $NaC_2H_3O_2$.

(*c*) *Basic Salts*.—In the case of POLY-ACID BASES, which contain more than one hydroxyl group replaceable by acid radicals, such as Cl, NO_3, SO_4, etc., BASIC SALTS may be formed by partial displacement of hydroxyl by acid, *e.g.*, Mg(OH)Cl and SbOCl.

Base.	*Basic salt.*	*Normal salt.*
MgO or $Mg(OH)_2$	Mg(OH)Cl	$MgCl_2$
Sb_2O_3 or $Sb(OH)_3$	SbOCl	$SbCl_3$

Variable Valency of Metals.

In applying this method to determine the formulæ of metallic salts, it is convenient to draw up a list of valencies of the metals as follows :—

Univalent	Li, Na, K, Ag, Cu′ (cuprous), Au′ (aurous), Hg′ (mercurous).
Bivalent	Mg, Ca, Sr, Ba, Cr″ (chromous), Mn″ (manganous), Fe″ (ferrous), Co, Ni, Cu″(cupric), Sn″ (stannous), Pb″ (plumbous), Zn, Cd, Hg″ (mercuric), Pt″ (platinous).
Tervalent	Al, Cr‴ (chromic), Fe‴ (ferric), Au‴ (auric), As, Sb, Bi.
Quadrivalent	Sn⁗ (stannic), Pb⁗ (plumbic), Th⁗ (thoric), Pt⁗ (platinic).

In this list several metals appear in more than one place. In such cases, the salts in which the metal has the lower valency are distin-

guished by the suffix *-ous*, whilst those of higher valency are distinguished by the suffix *-ic*, *e.g.*,

Stannous chloride,	$SnCl_2$
Stannic chloride,	$SnCl_4$
Ferrous chloride,	$FeCl_2$
Ferric chloride,	$FeCl_3$
Mercurous chloride,	$HgCl$ or Hg_2Cl_2
Mercuric chloride,	$HgCl_2$
Cuprous chloride,	$CuCl$ or Cu_2Cl_2
Cupric chloride,	$CuCl_2$
Aurous chloride,	$AuCl$
Auric chloride,	$AuCl_3$

Variable Valency of Non-metals. Nomenclature of Acids and Salts.

Similar names are applied in the case of the oxy-acids, when the valency of the non-metal in the acidic oxide varies. The acid containing the higher proportion of oxygen is then distinguished by the suffix *-ic*, *e.g.*, nitric acid, HNO_3, sulphuric acid, H_2SO_4, phosphoric acid, H_3PO_4, whilst that with less oxygen is distinguished by the suffix *-ous*, *e.g.*, nitrous acid, HNO_2, sulphurous acid, H_2SO_3, phosphorous acid, H_3PO_3.

Salts derived from an *-ic* acid are indicated by the suffix *-ate*, *e.g.*, nitrate, sulphate, phosphate, and salts derived from an *-ous* acid are indicated by the suffix *-ite*, *e.g.*, nitrite, sulphite, phosphite, whilst binary compounds of the metals with a single non-metal are indicated by the suffix *-ide*, *e.g.*, oxide, sulphide, chloride, nitride, phosphide, carbide, etc.

If still more oxygen is present, the prefix *per-* is attached to the name of the *-ic* acid or the *-ate* salt, whilst if still less oxygen is present the prefix *hypo-* is attached to the name of the *-ous* acid or the *-ite* salt.

Names and formulæ of typical series of acids and salts are shown in the following table:—

TABLE 22.—NOMENCLATURE OF ACIDS AND SALTS.

Acid.	*Salt.*
Hydrochloric acid, HCl	Sodium chloride, $NaCl$
Hypochlorous acid, $HClO$	Sodium hypochlorite, $NaClO$
Chlorous acid, $HClO_2$	Sodium chlorite, $NaClO_2$
Chloric acid, $HClO_3$	Sodium chlorate, $NaClO_3$
Perchloric acid, $HClO_4$	Sodium perchlorate, $NaClO_4$
Hyponitrous acid, $(HNO)_2$	Sodium hyponitrite, $(NaNO)_2$
Nitrous acid, HNO_2	Sodium nitrite, $NaNO_2$
Nitric acid, HNO_3	Sodium nitrate, $NaNO_3$

TABLE 22.—NOMENCLATURE OF ACIDS AND SALTS—(*continued*).

Acid.	*Salt.*
Sulphuretted hydrogen, H_2S	Sodium sulphide, Na_2S
Sulphurous acid, H_2SO_3	Sodium sulphite, Na_2SO_3
Sulphuric acid, H_2SO_4	Sodium sulphate, Na_2SO_4
Persulphuric acid, H_2SO_5	Sodium persulphate, $NaHSO_5$
Phosphoretted hydrogen, H_3P	Sodium phosphide, Na_3P
Hypophosphorous acid, H_3PO_2	Sodium hypophosphite, NaH_2PO_2
Phosphorous acid, H_3PO_3	Sodium phosphite, Na_3PO_3
Phosphoric acid, H_3PO_4	Sodium phosphate, Na_3PO_4
Perphosphoric acid, H_3PO_5	—

SUMMARY AND SUPPLEMENT.

1. The **atomic weight of a metal** cannot usually be determined by Avogadro's hypothesis, since very few metallic compounds are volatile. The atomic weights are therefore deduced by means of Dulong and Petit's **law of atomic heats**, according to which

atomic heat = *atomic weight* × *specific heat* = constant = 6·3 calories.

The approximate atomic weight is obtained by dividing the specific heat of the metal into 6·3; this gives the valency of the metal and shows by what integer the equivalent must be multiplied to give exact atomic weights.

2. The atomic weights of metals can also be deduced from the **law of isomorphism**, which states that

> "*Substances which are similar in crystalline form and in chemical properties can usually be represented by similar formulæ.*"

3. Metallic compounds are usually represented by **empirical formulæ**, the molecular weights being unknown. Structural formulæ are also more difficult to establish than in the case of compounds of carbon.

4. The **valency of a metal** is important as determining the formulæ of its salts. For this purpose, the valency may be defined as *the number of atoms of hydrogen which one atom of the metal will displace from an acid.*

CHAPTER XVI

THE MOLECULAR WEIGHTS OF DISSOLVED SUBSTANCES

Mixtures and Solutions.

When two substances are brought together they may either retain their individuality as in a MECHANICAL MIXTURE of sand and salt, or they may form a SOLUTION as in the case of salt and water, or finally they may form a new CHEMICAL COMPOUND as when hydrogen and oxygen burn to form water. In general, a chemical compound is distinguished from a solution or mixture by its fixity of composition and properties (Chapter III), whilst a solution differs from a mechanical mixture in the much more intimate blending of its components.

The term SOLUTION is applied primarily to those cases in which a gas or a solid, called the SOLUTE, is dissolved in a liquid, which is then described as the SOLVENT. The term "solution" may, however, be extended to all cases in which the blending of the components is as complete as when salt or sugar is dissolved in water, *e.g.*, it is legitimate to speak of the solution of gases in gases, or of gases and liquids in solids; and finally, when two isomorphous solids are blended together in homogeneous crystals, the product is often described as a SOLID SOLUTION.

Very minute particles of a solid may remain suspended for an indefinite time in a liquid, although they can be filtered out by a suitable membrane. They are then said to be in COLLOIDAL SOLUTION. The particles are usually too small to be seen under the microscope, but they may frequently be detected by the "ultramicroscope," in which each particle is revealed by a halo of light against a dark background. These colloidal solutions are intermediate in character between mechanical mixtures and true solutions; they differ profoundly from a mere suspension, say of sand in water, the difference increasing with the degree of DISPERSION, or minute subdivision, of the particles. When the dispersed material is a liquid instead of a solid, the mixture is described as an EMULSION.

Solutions of Gases in Liquids.

When an inert gas dissolves in a liquid there is a definite RATIO OF DISTRIBUTION of the gas between the liquid and gaseous layers, or

PHASES, as they are sometimes called (p. 187). This is expressed by HENRY'S LAW, which states that

"*The solubility of a gas is proportional to its pressure,*"

whilst DALTON'S LAW states that

"*In a mixture of gases the solubility of each gas varies proportionally with its partial pressure*"

and is independent of the presence of other gases. Thus water at 8° dissolves 2 per cent. of its volume of hydrogen or of nitrogen, or 4 per cent. of its volume of oxygen. If the pressure be doubled, the weight of gas in unit volume will be doubled both in the gas and in the solution, but the ratio of these weights will remain constant. From air, which contains 0·8 volume of nitrogen and 0·2 volume of oxygen, water will dissolve 0·8 × 2 = 1·6 per cent. of nitrogen and 0·2 × 4 = 0·8 per cent. of oxygen or, roughly, 2 parts of nitrogen to 1 of oxygen instead of 4 to 1 as in air.

When chemical combination takes place between a gas and a solvent Henry's law is no longer valid; *e.g.*, in the case of carbon dioxide, sulphur dioxide, ammonia, or chlorine, the action is disturbed by the formation of hydrates, as shown in the balanced equations

$$CO_2 + H_2O = H_2CO_3$$
$$SO_2 + H_2O = H_2SO_3$$
$$NH_3 + H_2O = (NH_4)OH$$
$$Cl_2 + 10H_2O = Cl_2{,}10H_2O.$$

When combination of this kind occurs, the solubility is increased, and the influence of pressure is usually greater than when no combination occurs; it is generally assumed, however, that there is still a definite ratio of distribution between the undissolved gas and that portion which is uncombined in the solution. The solubility of gases in liquids is usually diminished when the temperature is raised.

Mixtures of Liquids.

Many liquids, such as alcohol and water, may be mixed together in all proportions. When, however, paraffin and water are shaken together, the oil merely breaks up into tiny globules, which float to the surface when the mixture is allowed to stand, giving two liquid layers which will not mix permanently. When a little soap is added to the water, and the paraffin is squirted under the surface by means of a syringe, the globules formed by the "dispersion" of the oil may remain suspended indefinitely in the form of an EMULSION, just as butter-fat is suspended in milk; but the emulsion is destroyed immediately by the addition of a drop of acid, and with the aid of a microscope it is easy to see that the oil, instead of dissolving in the water, has merely been broken up and retained in the form of small globules.

A third case, intermediate between the two described in the preceding paragraph, namely, alcohol and water, and paraffin and water,

is illustrated by the behaviour of ether and water, which when shaken together separate into two layers as follows:—

Upper layer . .	Ether $97\frac{1}{3}$ per cent.	Water $2\frac{2}{3}$ per cent. at 20°
Lower layer . .	Water 93 per cent.	Ether 7 per cent. at 20°

If therefore a large amount of ether be taken and a small amount of water added, the water will dissolve completely; and, conversely, a small amount of ether will dissolve completely in a large quantity of water; but mixtures of intermediate composition will separate into two layers. Pairs of liquids such as these are said to be PARTIALLY MISCIBLE.

Melted solids behave in this respect exactly like other liquids. Thus, some metals such as lead and tin will mix together in all proportions when melted, whilst others such as lead and zinc are only partially miscible and when stirred up together separate into two layers, *e.g.*,

Upper layer . .	Zn 98·86 per cent.	Pb 1·14 per cent.
Lower layer . .	Pb 98·70 per cent.	Zn 1·30 per cent.

In this case the contrast between the two layers is easily seen, since the upper layer, consisting mainly of zinc, is hard and crystalline when solid, whilst the lower layer, consisting mainly of lead, is quite soft and malleable. Above 935°, however, lead and zinc will mix in all proportions.

Distribution between Liquids.

When a third substance is added to two layers of liquid, it usually distributes itself in a definite ratio between the two layers. The RATIO OF DISTRIBUTION (of which the solubility of gases is a special case) is, however, affected profoundly by chemical combination between the third substance and one of the liquids. Thus, in the case of ether and water, most metallic salts pass almost wholly into the water, with which they interact as described in Chapter XVIII, whilst oily substances, although they do not combine with the ether, show a strong preference for solution in this liquid. Mercuric chloride, however, gives a fairly even ratio of distribution of 2 : 1 for the concentrations in grams per litre in ether and in water; and alcohol distributes itself between equal volumes of ether and water in the ratio of approximately five-eighths in the ether to three-eighths in the water. Silver added to a mixture of lead and zinc gives a concentration approximately forty times as great in the zinc as in the lead, perhaps because it forms a series of chemical compounds with zinc, *e.g.*, AgZn, but not with lead.

The addition of a third substance which dissolves in both liquids has, however, the effect of diminishing the differences between them, so that finally the two layers become identical and mix in all proportions. It is therefore possible to prepare homogeneous ternary

mixtures of water, alcohol, and ether, or of lead, silver, and zinc, with a wide range of compositions in each case.

Molecular Weights of Dissolved Substances.

The determination of the molecular weights of gases by Avogadro's hypothesis depends on the fact that one of the physical properties of the gases, namely, their volume, depends only on the number of molecules that are present and not on their nature. Such properties are known as MOLECULAR PROPERTIES. By making use of certain similar properties of solutions, it is possible to extend the determination of molecular weights to dissolved substances, in addition to gases and vapours. Four properties used for this purpose are set out under (*a*) to (*d*) below, whilst the experimental methods are described in a later paragraph.

(*a*) *Lowering of Vapour-pressure.*—The vapour-pressure of a solvent is lowered by adding to it a solute which will not vaporise. The LOWERING OF THE VAPOUR-PRESSURE is in the ratio $\frac{p_0 - p}{p_0} = \frac{n}{N}$, where

p_0 is the vapour-pressure of the solvent,
p is the vapour-pressure of the solution,
N is the number of gram-molecules of the solvent,
n is the number of gram-molecules of the solute

in a given volume of the solution. This effect depends on the number and not on the nature of the molecules, and can therefore be used to compare molecular weights. Thus, the weights of two substances which produce an equal lowering of the vapour-pressure of water or of some organic solvent are proportional to their molecular weights.

The lowering of the vapour-pressure by a non-volatile solute can be explained readily by the KINETIC THEORY OF LIQUIDS (p. 132), according to which vapour-pressure is determined by an equilibrium between the evaporation of the liquid and the condensation of its vapour. The presence of the solute will not hinder the return to the liquid of molecules of the vapour which plunge into it, but it may prevent the escape of molecules from the liquid by occupying a portion of the free surface; in this way equilibrium will be reached at a lower concentration of the vapour than in the case of a pure solvent. This effect has been found to depend on the number and not on the nature of the molecules of the solute.

(*b*) *Elevation of Boiling-point.*—Since the vapour-pressure of a solvent is lowered by the presence of a non-volatile solute, it is clear that its boiling-point will be raised; thus, if the boiling-points are determined at atmospheric pressure, a rise of temperature will be needed to compensate for the lowering of the vapour-pressure below 760 mm. The ELEVATION OF THE BOILING-POINT is also a molecular property depending on the number and not on the nature of the molecules which are added to the solvent. The MOLECULAR ELEVATION, *i.e.*, the

elevation produced by one gram-molecule of solute, has the following values for 1000 grams of some common solvents.

TABLE 23.—MOLECULAR ELEVATION OF THE BOILING-POINT.

Substance.	*Boiling-point.*	*Molecular elevation.*
Water	+100°	0·52°
Benzene	+ 80·3°	2·6°
Alcohol	+ 78·8°	1·15°
Liquid sulphur dioxide . .	− 10°	1·50°

Thus, *m* grams of a solute of molecular weight *m* would be required to raise the boiling-point of 1000 grams of water from 100° to 100·52°. These constants can be determined either by calculation from the latent heat of evaporation (p. 171), or empirically, by measuring the effects produced by solvents of known molecular weight.

(*c*) *Depression of the Freezing-point.*—The freezing-point of a solvent is lowered by the presence of a solute which remains in solution when the solvent crystallises. The DEPRESSION OF THE FREEZING-POINT, which is familiar in the lower freezing-point of sea-water as compared with fresh-water, is also a molecular property, depending on the number but not on the nature of the molecules of the solute. The MOLECULAR DEPRESSION produced by one gram-molecule of solute in 1000 grams of some typical solvents is as follows :—

TABLE 24.—MOLECULAR DEPRESSION OF THE FREEZING-POINT.

Substance.	*Freezing-point.*	*Molecular depression.*
Water	0°	1·85°
Benzene	+ 5·5°	5·12°
Acetic acid	+16·6°	3·9°
White phosphorus . . .	+44°	32·2°

Thus, 46 grams of alcohol of molecular weight 46 would lower the freezing point of 1000 grams of water from 0° to −1·85°. These constants also can be calculated from the latent heat of fusion (p. 171) or deduced empirically by measuring the effects produced by solutes of known molecular weight.

(*d*) *Osmotic Pressure.*—The elevation of the boiling-point and depression of the freezing-point of a solution indicate that it is harder both to boil and to freeze the liquid, because work must be done in concentrating the solution, since in each case it is assumed that the solute remains dissolved whilst the pure solvent is being distilled out, or crystallised out, from the liquid. The work done can be calculated on the assumption that the concentration of the solution is

resisted (just like the concentration or compression of a gas) by a pressure. This pressure, which is known as the OSMOTIC PRESSURE of the solution, is also a molecular property of the solute. It can be determined directly by filtering the liquid through a SEMI-PERMEABLE MEMBRANE which will allow the solvent to pass but not the solute; *e.g.*, a membrane of copper ferrocyanide, $Cu_2FeC_6N_6$, built up in the walls of a porous tube or pot, can be used to retain the sugar in an aqueous solution of glucose, $C_6H_{12}O_6$, or sucrose, $C_{12}H_{22}O_{11}$, whilst allowing the water to pass through. The pressure which is just sufficient to drive the water through the membrane is taken as the osmotic pressure of the solution; this can also be determined by measuring the pressure that is set up when the tube is immersed in water, which then forces its way through the membrane and into the solution. In either case care must be taken to prevent any marked concentration or dilution of the solution by the water which is driven out or absorbed, since this would produce a change in the osmotic pressure of the solution in contact with the membrane.

Extension of Avogadro's Hypothesis to Solutions.

When the osmotic pressure of a solution has been determined, it is usually found to correspond with that which the solute would be expected to produce if its molecules were gaseous instead of dissolved. The calculation of molecular weights then depends on a direct extension of Avogadro's hypothesis, the only important change being the substitution of "osmotic pressure" for "gas pressure" in the calculations. A similar statement can be made in reference to the three preceding methods of determining molecular weights. Thus, assuming that the osmotic pressure of a solution is equal to the pressure exerted by a gas of the same concentration as the solute, the molecular elevation of the boiling-point and the molecular depression of the freezing-point can be calculated from the formula

$$E = \frac{1{\cdot}985\,(273 + t)^2}{1000\,W},$$

where E is the molecular elevation or depression, t is the boiling-point or freezing-point of the pure solvent, and W is its latent heat of vaporisation or fusion at this temperature. In all cases in which the constant calculated from this formula agrees with that found empirically, the molecular weights deduced from these measurements can be regarded as based directly upon Avogadro's hypothesis, modified only to the extent of replacing gas pressure by osmotic pressure.

Experimental Methods.

(*a*) *Lowering of Vapour-pressure.*—The apparatus shown in Fig. 59 was used by McBain to determine the lowering of the vapour-pressure of water by soap. The method depends on keeping the solution at a

constant temperature and determining the point to which its vapour must be cooled in order to deposit dew on a silver tube suspended in the vapour.

(*b*) *Depression of the Freezing-point.*—For determining the depression of the freezing-point a BECKMANN THERMOMETER, *D* (Fig. 60), is used, which is graduated on a very open scale to 0·01°, over a range of about 5°. The quantity of mercury in the bulb can be adjusted, for use with solvents of widely different freezing-points, by causing it to overflow into an auxiliary bulb at the top of the thermometer, where the surplus can be detached, or recovered again when the thermometer is set for a lower range of temperatures (compare inset, Fig. 61). The freezing-point is determined by "over-

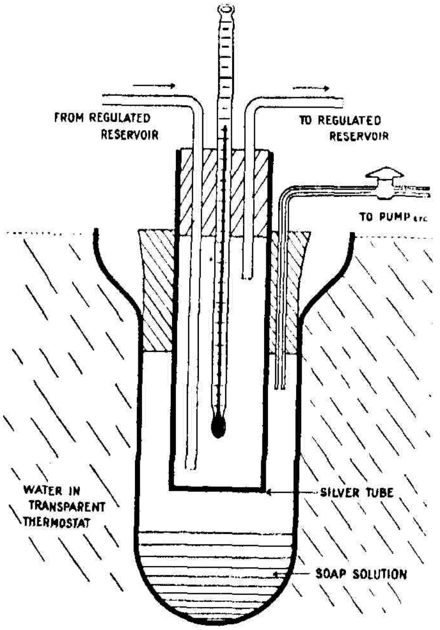


FIG. 59.—McBAIN'S APPARATUS FOR DETERMINING THE VAPOUR-PRESSURE OF SOAP-SOLUTIONS.

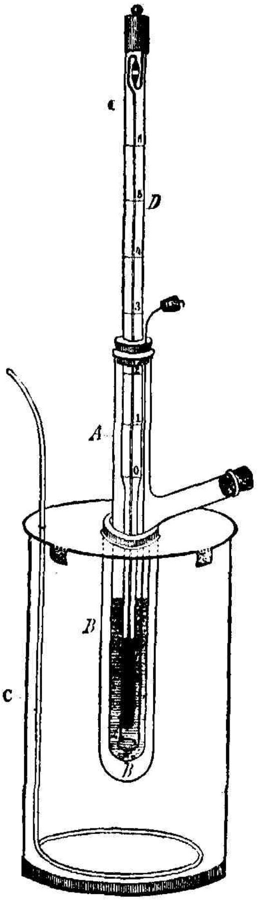


FIG. 60.—APPARATUS FOR DETERMINING THE DEPRESSION OF THE FREEZING-POINT OF SOLUTIONS, WITH BECKMANN THERMOMETER.

cooling" the solution in *A* to a temperature slightly below that at which crystallisation normally takes place. The liquid is then stirred vigorously to start the crystallisation and the highest reading of the

thermometer is taken as the INITIAL FREEZING-POINT of the solution. In order to prevent excessive cooling of the liquid, it is usually surrounded with an air-bath, *B*, and immersed in a bath of liquid, *C*, or in a freezing mixture, only slightly colder than the temperature which is to be observed.

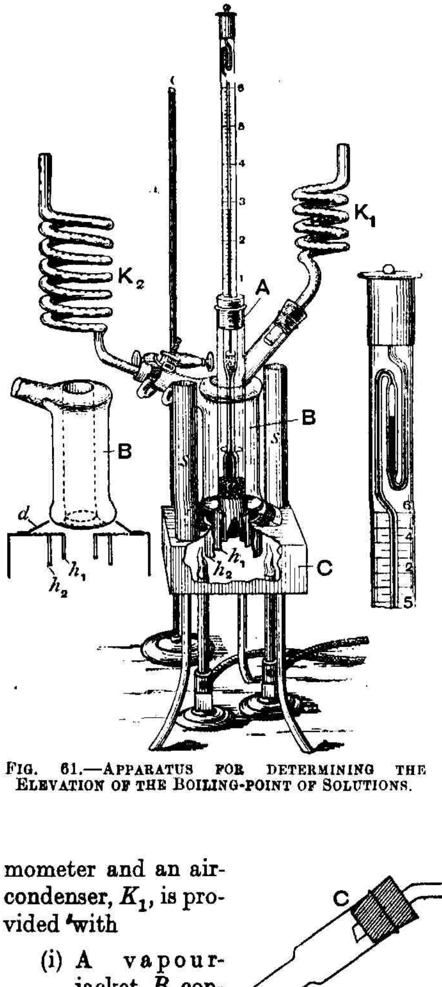


FIG. 61.—APPARATUS FOR DETERMINING THE ELEVATION OF THE BOILING-POINT OF SOLUTIONS.

(*c*) *Elevation of the Boiling-point.*—The principal difficulty here is to prevent over-heating of the liquid. For this purpose the boiling-tube, *A* (Fig. 61), carrying a Beckmann thermometer and an air-condenser, K_1, is provided with

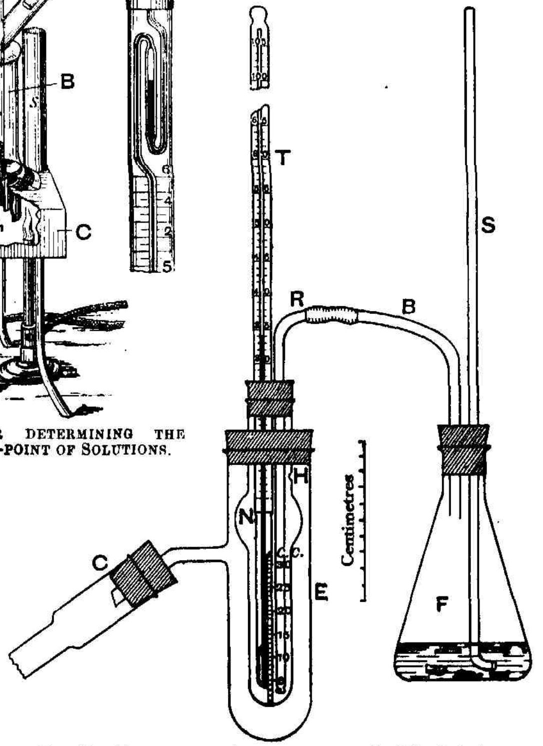


FIG. 62.—LANDSBERGER'S APPARATUS FOR DETERMINING BOILING-POINTS OF SOLUTIONS.

(i) A vapour-jacket, *B*, containing the pure solvent and fitted with an air-condenser, K_2.

(ii) A platinum peg passing through the bottom of the boiling-tube to conduct heat into the liquid.

(iii) A quantity of glass or agate beads to promote the formation and escape of bubbles.

Superheating of the liquid may be prevented even more effectively by passing the vapour of the pure solvent from a flask, *F* (Fig. 62), into the solution at *E* until the temperature is steady and then

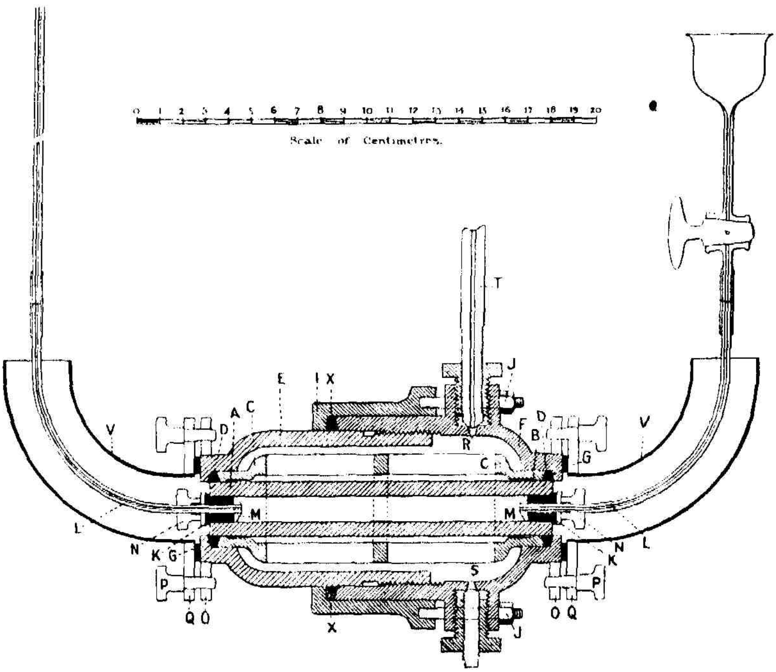


FIG. 63.—BERKELEY'S APPARATUS FOR MEASURING OSMOTIC PRESSURE.

AB is a porcelain tube, 15 cm. long, 2 cm. external and 1·2 cm. internal diameter, which carries a membrane of copper ferrocyanide near its outer surface; it is filled with water and surrounded by a concentrated solution of sugar in water. The space round the tube, where pressure is applied to the solution, is sealed by "dermatine" rings, *DD*, which are pressed against the gun-metal cage, *CC*, when the two parts, *EF*, of the outer gun-metal vessel are screwed together. The porcelain tube is closed by rubber stoppers, *KK*, compressed between metal washers, *MM*, and nuts, *NN*, so as to make tight joints with the brass capillary tubes, *LL*. These carry a glass funnel and a glass capillary tube which serves to record any flow of water through the membrane when pressure is applied through the tube, *T*, to the solution.

reading the temperature and determining either the volume or the weight of the solution (Landsberger's method). In the apparatus shown in Fig. 62 the vapour which has passed through the solution escapes through a small hole at *H* into a vapour-jacket before passing away to the condenser at *C*.

(*d*) *Osmotic Pressure.*—The apparatus required for making accurate measurements of osmotic pressure is too complex for use as a routine method of determining molecular weights. The apparatus used by Lord Berkeley to determine the pressure required to force water from a sugar solution through a membrane of copper ferrocyanide into the interior of a porous tube carrying the membrane is, however, shown in Fig. 63.

Applications.

By the methods described above, the molecular weights have been determined of a large number of substances which cannot be vaporised, since it is nearly always possible to find some solvent of definite boiling-point or freezing-point in which the molecular weight can be determined in solution. The method is, however, not generally applicable to metallic salts, since electrolytes (*i.e.*, solutions which conduct an electric current and are decomposed by it) give abnormal results, which are discussed in Chapter XVIII. In other cases, again, the molecular weight is found to vary with the concentration, on account of the ASSOCIATION of simple molecules into larger complexes as the concentration increases, or the converse process of DISSOCIATION on dilution.

Water is not a very common solvent for these determinations of molecular weight, but organic compounds such as benzene, C_6H_6, and acetic acid, $C_2H_4O_2$, are often used as solvents for compounds of carbon which cannot be vaporised conveniently; indeed, this method is often preferred to direct determinations of vapour density, which are much more troublesome to make. Molten phosphorus has been used as a solvent in determining the molecular weight of sulphur, and metals such as mercury, sodium, and lead have been used as solvents in determining the molecular weights of dissolved metals.

SUMMARY AND SUPPLEMENT.

1. **Solutions** are usually prepared by dissolving a **solute** (which may be a gas, liquid, or solid) in a liquid called the **solvent**; the solvent may also be an amorphous solid, such as rubber. Mixtures of gases may, however, be referred to as "solutions," and isomorphous mixtures of crystalline substances are often described as **solid solutions.** Minute particles of solid suspended in a liquid are described as being in **colloidal solution,** whilst minute particles of liquid suspended in a liquid form an **emulsion.**

2. The **solubility of gases in liquids** is controlled by *Henry's law,* which states that

"*The solubility of a gas is proportional to its pressure,*"

and by *Dalton's law,* which states that

"*In a mixture of gases the solubility of each gas varies proportionally with its partial pressure.*"

There is thus a constant **ratio of distribution** of the gas between the two layers. When the dissolved gas combines with the solvent there is still a definite ratio of distribution between the concentration c_1 in the gaseous layer

and the concentration c_2 of the *uncombined* gas in the liquid layer ; but most of the dissolved gas may be in a combined form, the concentration of which will depend on the character of the product.

3. A constant **ratio of distribution** is also observed when a third substance is distributed between two liquid layers or phases, *e.g.*, between ether and water or between zinc and lead. If, however, there is a difference of molecular weight in the two layers, or if a reversible chemical change takes place in one layer, the ratio of distribution can only be applied to those portions which are in a similar condition in the two layers. Thus when a solution of iodine in potassium iodide is shaken up with ether we have

$$\begin{array}{llcl} \textit{Ether} & \underset{c_1}{I_2} & & \\ \textit{Water} & \underset{c_2}{I_2} + \underset{c_3}{KI} & \rightleftharpoons & \underset{c_4}{KI_3} \end{array}$$

where c_1 and c_2 are the concentrations of the molecules of I_2 in the ether and in the water, c_3 is the concentration of the potassium iodide, KI, and c_4 the concentration of the tri-iodide, KI_3, in the aqueous layer. Here c_1/c_2 will be constant ; but the distribution of iodine between the two layers is given by $\frac{c_1}{c_2 + c_4}$, where $c_2 \times c_3 = kc_4$, and not by $\frac{c_1}{c_2}$.

4. The **molecular weights of dissolved substances** may be determined

(*a*) By the lowering of the vapour pressure of the solution.

(*b*) By the elevation of the boiling-point.

(*c*) By the depression of the freezing-point.

(*d*) By the osmotic pressure.

5. The **osmotic pressure** of a solution is usually equal to that which the solute would be expected to exert if it were present in the form of a gas. Molecular weights can therefore be deduced from measurements of osmotic pressure by a direct application of Avogadro's hypothesis in which osmotic pressure is substituted for gas pressure.

When this relationship between osmotic pressure and the calculated gas pressure holds good, the **molecular elevation of the boiling-point** and the **molecular depression of the freezing-point** can be calculated from the formula

$$E = \frac{1{\cdot}985\,(273 + t)^2}{1000\,W},$$

where t is the boiling-point, or freezing-point, of the pure solvent and W is its latent heat of vaporisation or fusion ; under these conditions the application of this formula can also be regarded as a mere extension of Avogadro's hypothesis from gases to solutions.

CHAPTER XVII

DISTILLATION AND CRYSTALLISATION OF LIQUID MIXTURES

Vapour Pressure of Mixtures.

Since the vapour pressure of a liquid is diminished by the presence of a solute (p. 169), the vapour pressure of a mixture of two liquids *A* and *B* may in general be expected to vary as shown in Fig. 64, where *PQ* and *RS* are the vapour pressures of *A* and *B*, whilst their partial pressures are shown as diminishing to zero along the lines *PS* and *RQ* as the proportion of *A* or *B* in the mixture decreases from 100 to 0 per cent.

(*a*) In an ideal case, if the relative numbers of molecules of *A* and *B* are plotted along the line *QS*, the partial pressures will be shown by two straight lines *PS* and *RQ* (Fig. 64*a*), and the vapour pressure of the mixtures, which is the sum of the partial pressures, will be shown by a straight line running across from *P* to *R*

(*b*) If *A* and *B* have a strong attraction for one another, the vapour pressure will be diminished much more rapidly, as in Fig. 64*b*. A MIXTURE OF MINIMUM VAPOUR PRESSURE OF MAXIMUM BOILING-POINT may then be formed as in the case of

	Acid.	*Boiling-point.*
Sulphuric acid and water . .	98·7% H_2SO_4	338°
Nitric acid and water . .	68% HNO_3	120·5°
Hydrogen chloride and water .	20·24% HCl	110°

(*c*) When the liquids have very little attraction for one another, on the other hand, a MIXTURE OF MAXIMUM VAPOUR PRESSURE OF MINIMUM BOILING-POINT may be formed as in the case of

Alcohol 95·59 per cent. Water 4·41 per cent. Boiling-point 78·13°.

This case is shown in Fig. 64*c*. In extreme cases the liquids have so little attraction for one another that they do not even mix completely, but separate into two layers; since these are in equilibrium with one another, their partial and total vapour pressures must be equal. Finally, if the liquids do not mix at all, but merely float one on the other, the vapour pressure of the mixture will be the sum of the separate vapour pressures of the components.

Distillation of Liquid Mixtures.

By fractional distillation a mixture of two liquids can be separated into

(i) Two pure liquids (Fig. 64*a*).
(ii) One pure liquid and a mixture of maximum boiling-point (Fig. 64*b*).
(iii) A mixture of minimum boiling-point and a pure liquid (Fig. 64*c*).

The completeness of the separation depends in each case on the efficiency of the still-head or fractionating column (p. 21). Tests with a number of different still-heads are shown in Fig. 22 (p. 23).

Formation of Glassy Solids.

When a viscous liquid is cooled, it usually solidifies in an amorphous condition, as a GLASS, without any segregation of its components. This solidification is gradual, since there is no abrupt change of pro-

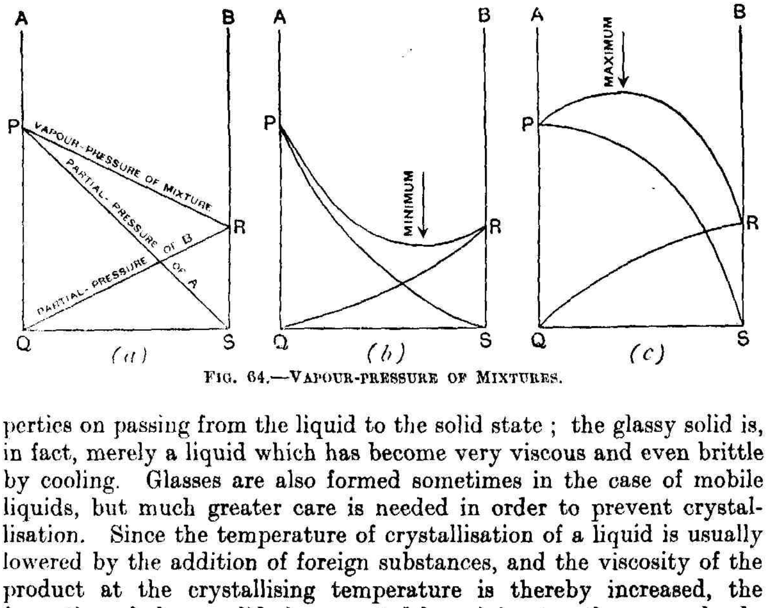


FIG. 64.—VAPOUR-PRESSURE OF MIXTURES.

perties on passing from the liquid to the solid state ; the glassy solid is, in fact, merely a liquid which has become very viscous and even brittle by cooling. Glasses are also formed sometimes in the case of mobile liquids, but much greater care is needed in order to prevent crystallisation. Since the temperature of crystallisation of a liquid is usually lowered by the addition of foreign substances, and the viscosity of the product at the crystallising temperature is thereby increased, the formation of glassy solids is promoted by mixing together several substances ; thus commercial glasses (p. 496) are mixtures of silicates of lime, soda, potash, etc., often with borates and phosphates as additional components.

At all temperatures below the normal temperature of crystallisation, the glassy state is metastable, that is, it may persist for a long time, but it always tends to revert to the more stable crystalline state. This reversion becomes more and more rapid as the temperature is raised,

or amorphous material by straining the metal and so destroying in part its crystalline character. Such treatment renders the metal hard and brittle, especially in the case of alloys. The softer metals, such as tin and lead, revert quickly to the original crystalline form; but in other cases the hardness persists indefinitely until it is removed by ANNEALING the metal, *i.e.*, by heating it to a temperature (usually from 150° to 300°) at which recrystallisation can take place.

Crystallisation of Liquid Mixtures.

The cooling of a liquid normally results in crystallisation, whether the liquid be a pure substance or a mixture. In a pure substance crystallisation takes place at a constant temperature as in the freezing of water at 0°, but the crystallisation of a mixture may be spread out over a wide range of temperatures. Crystallisation at constant temperature may, however, occur in a liquid mixture if the solid which separates has the same composition as the liquid, *e.g.*, if the solid is

(i) An isomorphous mixture or solid solution (p. 11).
(ii) An "eutectic" mixture (p. 182).
(iii) A chemical compound crystallising from a mixture of the same composition.

Much information as to the nature of the solid which separates from a liquid mixture may be obtained from a study of a FREEZING-POINT CURVE showing the temperature at which crystallisation begins in mixtures of different composition. The three principal cases, including the crystallisation of isomorphous mixtures, eutectic mixtures, and chemical compounds, are described in detail in the three following paragraphs.

Crystallisation of Isomorphous Solids.

(*a*) In some cases liquids which will mix in any proportions retain this property when solid, and give rise to a complete series of isomorphous crystals or solid solutions on crystallisation (p. 11). These are frequent amongst minerals, especially in igneous rocks derived from a magma containing the isomorphous oxides, Al_2O_3, Fe_2O_3, and Cr_2O_3, or MgO, CaO, and FeO, or Na_2O and K_2O. Examples are also found amongst alloys, *e.g.*,

gold and *silver*
palladium and *silver*
platinum and *gold*

These pairs of metals will form homogeneous crystals or solid solutions when melted together in any proportions.

(*b*) The formation of isomorphous mixtures on cooling a liquid is shown

(i) *By the absence of segregation*, only one type of crystal being seen when the mixture or alloy is examined.

(ii) *By a continuous variation of properties, as the composition of the mixture is changed.* Thus, the *density* varies progressively from that of one pure substance to that of the other, and the *freezing-point* of the whole series of alloys is represented by a continuous curve as in Fig. 67.

The solid which crystallises is not necessarily of exactly the same composition as the liquid; the LIQUIDUS curve, showing the temperature at which crystallisation begins in liquids of different composition, and the SOLIDUS, showing the composition of the solid which separates from the liquid at different temperatures, need not therefore coincide, although the separation is usually slight.

Fig. 67 shows the freezing-point curves for (*a*) gold and silver, (*b*) palladium and silver, (*c*) platinum and gold. In (*a*) the liquidus and solidus are too close together to be shown separately in the diagram and the solid has almost exactly the same composition as the liquid from which it separates. In (*c*), on the contrary, the liquidus and solidus are widely separated; if a horizontal line be drawn to represent any arbitrary temperature of crystallisation, it will intersect the solidus at a point on the diagram which approaches much nearer to the "platinum" axis on the left hand than does its intersection with the liquidus; the solid which separates at this temperature is therefore much richer in platinum than the liquid from which it separates. It should be noted that during crystallisation there is no marked difference of temperature between the liquid and solid: the space between the liquidus and solidus may therefore be ruled with horizontal lines, the ends of which show the compositions of liquid and solid which are in equilibrium with one another. In the same way in Fig. 121 (*a*) (p. 277), a *liquid*, *b*, containing 50 atoms per cent. of bromine deposits at $-52°$ crystals, *c*, containing 64 atoms per cent. of this element, whilst a *solid*, *a*, containing 50 atoms per cent. of bromine is in equilibrium at $-66°$ with a liquid, *d*, containing only 36 atoms per cent. of bromine.

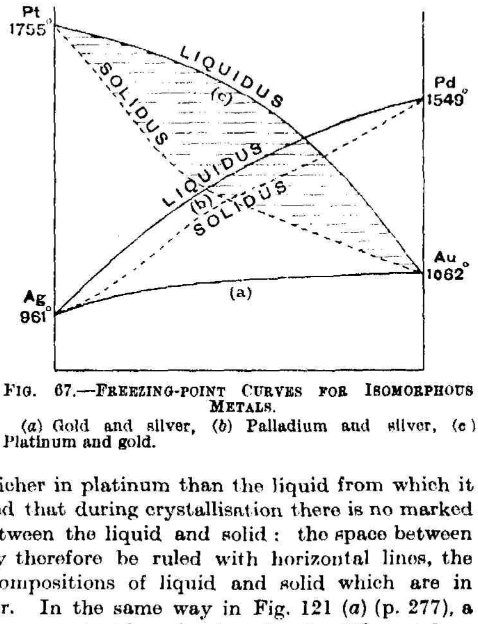


FIG. 67.—FREEZING-POINT CURVES FOR ISOMORPHOUS METALS.
(*a*) Gold and silver, (*b*) Palladium and silver, (*c*) Platinum and gold.

(*c*) Isomorphous mixtures or solid solutions are sometimes formed from substances which are dissimilar in their usual crystalline forms. Thus, "blue vitriol" or copper sulphate, $CuSO_4,5H_2O$, will carry down from solution an isomorphous pentahydrate, $FeSO_4,5H_2O$, of ferrous sulphate, although this salt usually crystallises as "green

vitriol" with $7H_2O$. In the same way, although mercury and cadmium have different crystalline forms, they give two series of solid solutions, those containing less than 51 per cent. of cadmium being isomorphous with mercury, whilst those containing more than 51 per cent. of cadmium are isomorphous with cadmium (Fig. 68). In such cases each constituent is potentially dimorphous, and the phenomenon is known as ISODIMORPHISM.

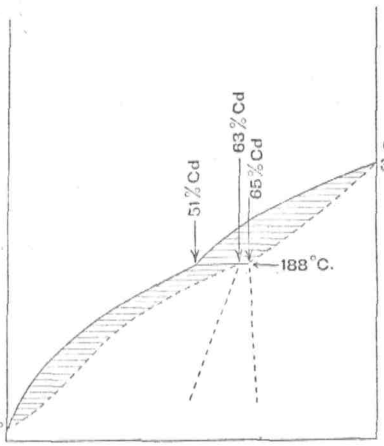


FIG. 68.—ISODIMORPHISM OF MERCURY AND CADMIUM.

In Fig. 68 the liquidus (shown as a full line) covers the whole range of compositions from 100 per cent. Hg to 100 per cent. Cd, the two sections of the liquidus intersecting at 51 per cent. Cd. The solidus (shown by dotted lines) is discontinuous, the first series of crystals, isomorphous with mercury, extending from 0 to 63 per cent. Cd, whilst the second series, isomorphous with cadmium, extends from 65 per cent. to 100 per cent. Cd.

Crystallisation of Eutectics.

(*a*) *Eutectic Mixtures.*—In most cases the solid which separates first from a liquid mixture consists of one of the components in a pure state, *e.g.*, salt water deposits fresh ice; but the INITIAL FREEZING-POINT, at which crystallisation begins, is lowered by the presence of the second substance, provided that this is not isomorphous with the first. When the initial freezing-points of a series of mixtures of this type are plotted, the freezing-point of each substance is represented by a descending line, and these descending lines must ultimately intersect,

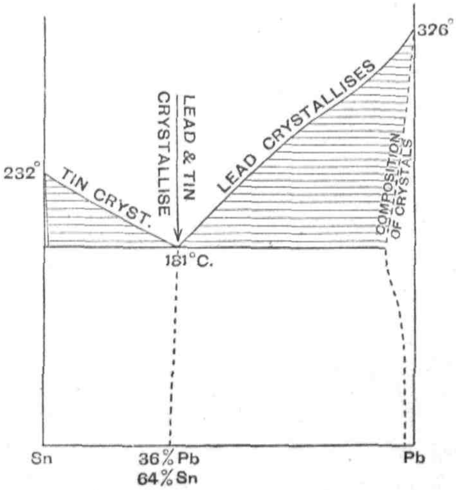


FIG. 69.—FREEZING-POINT DIAGRAM FOR TIN AND LEAD.

forming a V-shaped curve as in Fig. 69. The minimum on this curve, at which intersection takes place, shows the composition of the EUTECTIC MIXTURE or EUTECTIC ALLOY, from which both components crystallise with equal readiness at the lowest freezing-point of the whole series. The eutectic has a definite composition and crystallises at a constant temperature, just like a pure substance, and with so little segregation that high magnification is usually required to reveal the constituents. The constant composition of the eutectic, and its crystallisation at

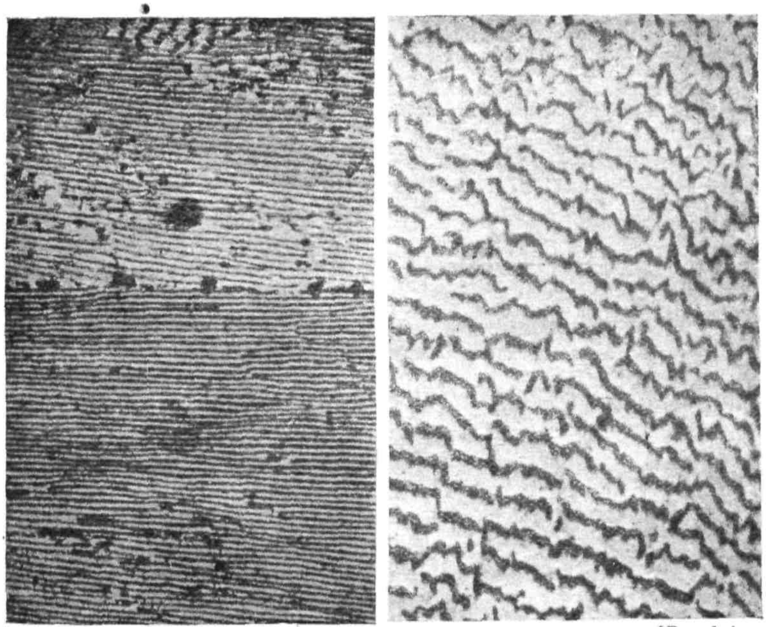


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FIG. 70.—EUTECTIC ALLOY OF TIN AND LEAD.

(White = tin, black = lead.) Notice the predominance of tin in the eutectic alloy.

constant temperature, suggest that it might be a chemical compound but it is proved to be a mixture and not a compound

(i) by the fact that the composition, although fixed by the intersection of two lines on the diagram, does not usually correspond with any simple formula ;

(ii) by the fact that the separate components can be seen, *e.g.*, by examination under a microscope (Figs. 70 and 71 (*a*) and Fig. 252, p. 708), although the segregation may be so slight that a high magnification is required to reveal them.

(*b*) *Tin and Lead.*—The freezing-point diagram for tin and lead is shown in Fig. 69, whilst the appearance of the eutectic alloy, which is

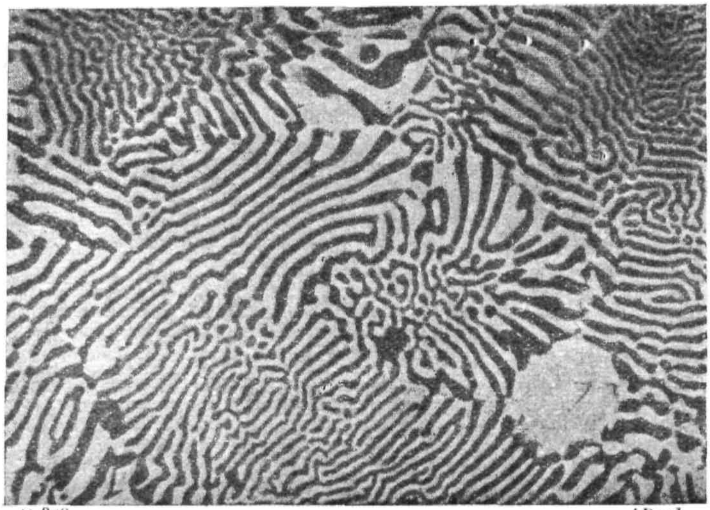

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FIG. 71 (*a*).—EUTECTIC ALLOY OF COPPER (black) AND COPPER PHOSPHIDE (white).

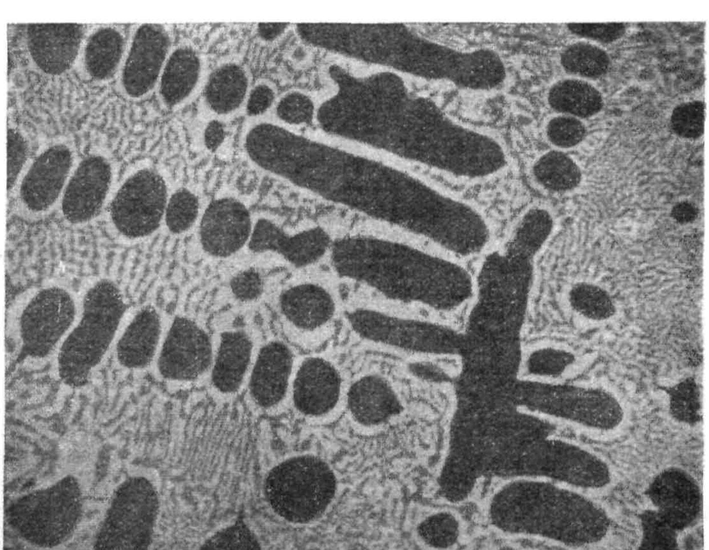

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FIG. 71 (*b*).—ALLOY OF COPPER AND COPPER PHOSPHIDE (Copper in excess).

used as a SOFT SOLDER, is shown in Fig. 70. Other alloys of tin and lead deposit the excess of either metal (above the proportion required to produce the eutectic mixture) in large crystals as the alloy cools from the initial freezing-point to the eutectic temperature. If these crystals are sufficiently large, the eutectic alloy may then be poured off as a liquid, as in the purification of copper by liquation ; but if cooled further it solidifies at the eutectic temperature to a matrix in which the larger crystals of the excess metal are embedded. In this series of alloys the tin separates in a state of almost complete purity, and the solidus corresponding with that part of the liquidus where tin crystallises almost coincides with the vertical axis for 100 per cent. Sn ; but the lead carries down with it a small proportion of tin and gives a sloping solidus as shown by the dotted line labelled " composition of crystals " in Fig. 69.

Fig. 71 shows at (*a*) the eutectic alloy of copper (black) and copper phosphide, Cu_3P (white). At (*b*) the same alloy is shown but with an excess of copper ; this has separated out, in advance of the eutectic, in large black " crystallites." When copper phosphide is in excess the structure of the alloy is similar, but the " crystallites " of the phosphide are white. Notice the rounded boundaries of the crystallites and their regular orientation (" fir-tree pattern ") ; also notice the white areas surrounding the grains of copper, which have attracted to themselves all the copper in their immediate neighbourhood, leaving a small region containing only copper phosphide.

(*c*) *Solutions.*—When one of the components of the mixture is a liquid, and the other a solid, as in the case of water and salt (Fig. 72), one arm of the eutectic diagram forms a FREEZING-POINT CURVE for the liquid, whilst the other arm forms a SOLUBILITY CURVE for the solid, and shows the temperatures at which crystals begin to separate from solutions of given composition. When a solution of salt in water is cooled, the excess of salt or of ice crystallises out first, and finally the eutectic mixture of ice and salt, which contains 22·4 per cent. of NaCl, crystallises at − 21·2°. Below this temperature only solid products are obtained, and this is therefore the lowest temperature which can be reached by mixing ice and salt to produce a FREEZING-MIXTURE.

Crystallisation of Chemical Compounds.

(*a*) *Salt and Water.*—In many cases a chemical compound crystallises from the liquid mixture ; thus, a dihydrate, $NaCl,2H_2O$, of common salt separates from aqueous salt solutions at temperatures below 0·15°. This hydrate is more stable than the anhydrous salt at all temperatures below 0·15°, the full curve for the dihydrate in Fig. 72 running above the broken curves for anhydrous salt and ice ; thus, when the hydrate is not formed the eutectic mixture contains more salt and crystallises at a lower temperature, as shown by the broken V in Fig. 72. Above 0·15° this condition is reversed ; the hydrate is now more soluble and decomposes into water and the anhydrous salt, so that only the latter is deposited from solution.

(ii) *Two* phases can exist in equilibrium with one another over a range of temperatures, each corresponding with a definite pressure, as represented by a *line* in the equilibrium-diagram.

(iii) *One* phase can exist over a range of temperatures and pressures, represented by an *area* in the diagram.

This application of the phase rule may be verified by referring to the diagram for steam, water, and ice (Fig. 7, p. 7).

In general the phase rule states that when the number of MOLECULAR SPECIES, *i.e.*, of independent materials brought into equilibrium with one another, is increased from 1 to n, the number of phases (vapour, liquid, crystalline solid, etc.) required to produce these conditions is as follows :—

(i) *Invariant system* (p and T both fixed) $n + 2$ phases.
(ii) *Univariant systems* (p and T vary together) $n + 1$ phases.
(iii) *Bivariant systems* (p and T can vary independently) n phases.

Thus, in mixtures of ice and salt, where two molecular species are present ($n = 2$),

(i) $n + 2 = 4$ phases, *e.g.*, ice, salt, solution, and vapour, can co-exist only at one temperature and one pressure, namely, at the eutectic temperature and under the vapour pressure of the eutectic at that point.

(ii) $n + 1 = 3$ phases, *e.g.*, solid salt, saturated solution, and vapour, can co-exist under a definite vapour pressure at each temperature.

(iii) $n = 2$ phases, *e.g.*, unsaturated solution and vapour can co-exist over a range of temperatures and pressures.

SUMMARY AND SUPPLEMENT.

1. **Vapour Pressure of Mixtures.**—The vapour pressure of two liquids may

(*a*) *Increase progressively* from one pure substance to the other, in which case the liquids can be separated by fractional distillation.

(*b*) *Pass through a minimum*, if the two liquids have a strong attraction for one another, giving rise to a mixture of maximum boiling-point, *e.g.*,

Sulphuric acid,	H_2SO_4, 98·7 per cent., b.-pt. 338°
Nitric acid,	HNO_3, 68 per cent., b.-pt. 120·5°
Hydrochloric acid,	HCl, 20·24 per cent., b.-pt. 110°.

(*c*) *Pass through a maximum*, giving a mixture of minimum boiling-point as in the case of

Alcohol 95·59 per cent. ; *water* 4·41 per cent. ; b.-pt. 78·13°.

2. **Crystallisation of Liquid Mixtures.**—These may give

(*a*) *Isomorphous mixtures*, indicated by a continuous freezing-point curve, *e.g.*,

Pt with Fe, Cu or Au (Fig. 67),
Pd with Cu, Ag (Fig. 67), or Au,
Au with Ag (Fig. 67),
Ni with Fe, Co, or Cu (Figs. 265 and 273),
Bi with Sb;

in exceptional cases the continuous curve may pass through a shallow minimum, *e.g.*, Fe with V, Cu with Au (Fig. 276) or Mn, Cr with Co or Ni (Fig. 273), Mn with Ni or Cu (Fig. 256); more rarely a maximum is observed, *e.g.*, Mn with Mn_3C (Fig. 255).

(*b*) *An eutectic alloy*, indicated by the intersection of the freezing-point curves of the two components, forming a V-shaped diagram, *e.g.*,

Salt and water,
Tin and lead,

and many other mixtures of substances that are not isomorphous.

(*c*) *Chemical Compounds.*

(i) If the compound is not isomorphous with its components, but forms eutectics with them, a W-shaped freezing-point curve is produced. In exceptional cases there may be several maxima, each corresponding with the composition of a definite compound. More frequently intersecting curves are obtained, each section corresponding with a definite compound, which decomposes and gives place to another before its melting-point is reached.

(ii) If the compound is isomorphous with its components, a continuous freezing-point curve may be produced, *e.g.*,

Br	BrI	I	(Fig. 128).
Li	LiCd	Cd	
Mg	MgCd	Cd	

In the second of these cases the curve passes through a maximum, corresponding with the composition of the compound.

3. **The phase rule** states that "In a system containing n molecular species,

(*a*) $n + 2$ *phases* can only exist in *invariant systems*, in which the pressure and temperature are both fixed.

(*b*) $n + 1$ *phases* can exist together in a *univariant system*, in which p and T may vary but not independently.

(*c*) n *phases* or less can exist in a *bivariant system* in which temperature and pressure can vary independently of one another."

These statements may be verified in the case of water, where $n = 1$, or of water and salt, where $n = 2$.

CHAPTER XVIII

THE PROPERTIES OF SALT SOLUTIONS

Electrical Conductivity of Salt Solutions.

Aqueous solutions of metallic salts are usually ELECTROLYTES, *i.e.*, they possess the property of carrying the electric current and of being decomposed thereby. This property is also possessed by molten salts, as well as by salts dissolved in certain other solvents, such as alcohol, pyridine, anhydrous prussic acid, etc., instead of in water.

Under the influence of the electric current the salt undergoes ELECTROLYSIS (Latin, *electrum*, amber; Greek, λύσις, a loosening) and is resolved into radicals of two kinds, namely,

(i) *The positive or metallic radical, e.g.*, Na, Ca, NH_4, etc.
(ii) *The negative or non-metallic radical, e.g.*, Cl, CN, SO_4, etc.

The positive radicals are carried with the current and liberated at the CATHODE (Greek, κατά, down; ὁδός, way), *i.e.*, the electrode where the current leaves the liquid; the negative radicals are carried in the opposite direction and are set free at the ANODE (Greek, ἀνά, up; ὁδός, way), where the current enters the liquid.

Primary and Secondary Products of Electrolysis.

In the case of a binary salt, such as sodium chloride, the *primary products* of electrolysis are SIMPLE RADICALS containing only one element such as sodium or chlorine; but in other compounds these are replaced by COMPOUND RADICALS containing more than one element, as in the ammonium salts, cyanides, nitrates, ferrocyanides, etc.

Sodium chloride	$NaCl$	$\longrightarrow$	Na	+	Cl
Ammonium chloride	NH_4Cl	$\longrightarrow$	NH_4	+	Cl
Sodium cyanide	$NaCN$	$\longrightarrow$	Na	+	CN
Sodium nitrate	$NaNO_3$	$\longrightarrow$	Na	+	NO_3
Potassium ferrocyanide	$K_4FeC_6N_6$	$\longrightarrow$	$4K$	+	FeC_6N_6

When these primary products are liberated at the electrodes they frequently undergo decomposition or chemical change, giving rise to

secondary products, e.g., by interacting (*a*) with one another, (*b*) with the electrode, (*c*) with the electrolyte.

(*a*) *Polymerisation.*—When molten silver chloride is electrolysed between a silver cathode and a carbon anode,

$$AgCl = Ag + Cl,$$

the silver atoms appear, perhaps without chemical change, as *metallic silver*, but the chlorine atoms unite in pairs to form molecules of *chlorine gas*.

$$Cl + Cl = Cl_2.$$

In the same way, when a cyanide is electrolysed we have at the anode the formation of *cyanogen gas* from pairs of cyanogen radicals,

$$CN + CN = C_2N_2.$$

So also, the electrolysis of fairly strong sulphuric acid gives *hydrogen gas* at the cathode and *perdisulphuric acid* at the anode as shown in the following equations :—

Primary decomposition :

$$H_2SO_4 = H + HSO_4.$$

Secondary change :

At the cathode $H + H = H_2$

At the anode $HSO_4 + HSO_4 = H_2S_2O_8$ (Perdisulphuric acid)

(*b*) *Attack on the Anode.*—In other cases the anode is attacked by the negative radical, as, for instance, (i) when silver nitrate is electrolysed in a silver voltameter (Fig. 74), (ii) when copper sulphate is electrolysed between copper plates (Fig. 75), or (iii) lead nitrate between lead plates.

(i) $NO_3 + Ag = AgNO_3$. (ii) $SO_4 + Cu = CuSO_4$. (iii) $2NO_3 + Pb = Pb(NO_3)_2$.

In these cases the negative radicals dissolve from the anode just as much metal as is deposited at the cathode, so that at the end of the action the composition of the solution is unchanged, but a transfer of metal has taken place from the anode to the cathode.

(*c*) *Interaction with the Electrolyte.*—In other cases the primary products interact with the electrolyte, as at the cathode in the electrolysis of brine,

Primary decomposition :

$$NaCl = Na + Cl.$$

Secondary changes :

At the anode $Cl + Cl = Cl_2$

At the cathode $2Na + 2H_2O = 2NaOH + H_2$

or at the anode in the electrolysis of lead nitrate between platinum electrodes, where plumbic nitrate is perhaps an intermediate stage in the production of lead peroxide.

Primary decomposition :

$$Pb(NO_3)_2 = Pb + 2NO_3.$$

Secondary changes at the anode :

$2NO_3 + Pb(NO_3)_2$ (Plumbous nitrate) $= Pb(NO_3)_4$ (Plumbic nitrate)

$2H_2O + Pb(NO_3)_4$ (Plumbic nitrate) $= PbO_2$ (Lead peroxide) $+ 4HNO_3$.

Faraday's Two Laws of Electrolysis.

The relationship between the current used and the decomposition produced is expressed in FARADAY'S TWO LAWS OF ELECTROLYSIS.

(*a*) FARADAY'S FIRST LAW OF ELECTROLYSIS states that :

" *The amount of decomposition is proportional to the total current that passes through the electrolyte.*"

This law implies that the amount of decomposition is independent of the temperature, concentration, and current-density, and of all other extraneous conditions such as the form of the apparatus used for the decomposition. It has been verified over a wide range of conditions in the electrolysis of silver nitrate (Fig. 74), which has indeed been made the basis of the international definition of the unit of electrical current ; thus the AMPERE is defined as that current which, when passed through an aqueous solution of silver nitrate under certain specified conditions, deposits 1·118 mg. of silver per second. In this case the conditions of the electrolysis are specified in order to avoid secondary changes which may occur, for instance, when the current-density is too high or the solution impure.

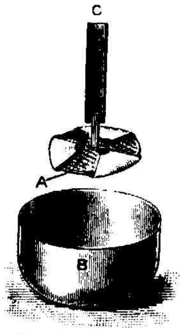


FIG. 74.- SILVER VOLTAMETER.

The silver voltameter (Fig. 74), as used for measuring currents of about 1 ampere, consists of a platinum bowl, *B*, not less than 10 cm. in diameter, serving as the cathode, and a silver plate, *A*, with a silver strip riveted to it, wrapped in filter-paper and mounted on a brass rod, *C*, serving as the anode. The electrolyte, which is poured into the bowl, is an aqueous solution of silver nitrate containing 15 per cent. of the salt. During electrolysis the silver plate is clamped in the centre of the bowl, the filter-paper (secured with sealing wax) being used to prevent any particles of metal detached from the anode from falling into the bowl. The deposit of silver in the bowl is washed, soaked for at least six hours, and then rinsed with distilled water and with alcohol and dried at 160° before weighing.

(*b*) FARADAY'S SECOND LAW OF ELECTROLYSIS states that :

" *When different compounds are decomposed by the same current, equivalent quantities of the various products are obtained.*"

This law enables us to calculate from the data for silver the weight of any other metal which would be deposited by the same current. Thus, the ELECTROCHEMICAL EQUIVALENTS of silver, copper, and hydrogen, *i.e.*, the weight of these elements deposited by one ampere in one second, must be proportional to their chemical equivalents,

107·88, 31·78, and 1·008. Since 1 ampere deposits 1·118 mg. of silver per second, the ELECTROCHEMICAL EQUIVALENT OF SILVER is, by definition, 0·001118 gram per coulomb.* By means of Faraday's Second Law the ELECTROCHEMICAL EQUIVALENT OF COPPER can be calculated to be

$$0{\cdot}001118 \times \frac{31{\cdot}78}{107{\cdot}88} = 0{\cdot}0003293 \text{ gram per coulomb},$$

whilst the ELECTROCHEMICAL EQUIVALENT OF HYDROGEN is

$$0{\cdot}001118 \times \frac{1{\cdot}008}{107{\cdot}88} = 0{\cdot}00001044 \text{ gram per coulomb}.$$

In general it may be stated that one gram-equivalent of any compound will be decomposed by the passage of $\frac{107{\cdot}88}{0{\cdot}001118} = 96{,}540$ coulombs of current.

The copper voltameter (Fig. 75) consists of an anode, *A*, of sheet copper, a bath of copper sulphate, *B*, and a copper cathode, *C*. During electrolysis copper is removed from the anode, *A*, and deposited on the cathode, *C*; the increase in weight of *C* (which should be equal to the loss in weight of *A*, if *A* consists of pure copper) is a measure of the total current that has passed through the voltameter.

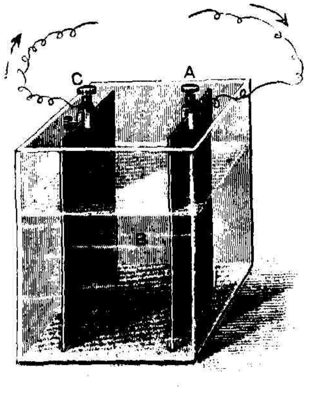


FIG. 75.—COPPER VOLTAMETER.

The Theory of Ions.

The fact that each equivalent of material set free in electrolysis is accompanied by a constant quantity of electricity suggested to Faraday that the atoms or groups of atoms into which the salt is resolved by electrolysis must carry with them a definite charge, which is liberated on reaching the electrode. These charged radicals were described by Faraday as IONS (Greek ἰόν, going). The metallic radical with its positive charge is known as the CATION (Greek κατά, down; ἰόν, going). The non-metallic radical with its negative charge is known as the ANION (Greek ἀνιόν, going up).

The charge on an ion is proportional to its valency. Thus,

* The coulomb is the unit of quantity, where the ampere is the unit of current. 1 coulomb = 1 ampere-second.

in the case of a few typical salts the ions are represented as follows :—

$$NaCl \longrightarrow \overset{+}{Na} + \overset{-}{Cl}$$
$$CuCl_2 \longrightarrow \overset{++}{Cu} + 2\overset{-}{Cl}$$
$$Na_2SO_4 \longrightarrow 2\overset{+}{Na} + \overset{--}{SO_4}$$
$$CuSO_4 \longrightarrow \overset{++}{Cu} + \overset{--}{SO_4}$$

the unit charge of 96,540 coulombs per equivalent being represented by the sign + or —.

Energy Required for Electrolysis.

The decomposition of a salt by electrolysis involves an absorption of ELECTRICAL ENERGY which can be expressed as the product of the ELECTROMOTIVE FORCE (or " voltage ") required to bring about the electrolysis and the TOTAL CURRENT in coulombs required to decompose one equivalent of the salt, thus

work done = *volts* × *coulombs* = *volts* × *amperes* × *seconds.*

Since, by Faraday's Second Law, the total current required to decompose one equivalent of a salt is constant, it follows that the *E.M.F.* is a direct measure of the force required to effect the decomposition.

In order to calculate the theoretical electromotive force, it is necessary to know the amount of heat-energy, Q, that is liberated in the formation of one equivalent of the salt from its products of decomposition. This should be equal to the electrical energy, E, required for its decomposition. Thus, by introducing the MECHANICAL EQUIVALENT OF HEAT (1 calorie = $4{\cdot}189 \times 10^7$ ergs, compare p. 128), and remembering that 1 volt × 1 coulomb = 1 joule = 10,000,000 ergs, we have for a decomposition which requires V volts and liberates H calories per equivalent on combination,

$$E = V \times 96{,}540 \text{ joules} = V \times 96{,}540 \times 10^7 \text{ ergs and}$$
$$Q = H \text{ calories} = H \times 4{\cdot}189 \times 10^7 \text{ ergs.}$$

Equating these two quantities, $E = Q$, and dividing out, we find that

$$V \times 23050 = H,$$

i.e., 1 *volt is equivalent to a heat-liberation of* **23050** *calories per equivalent.**

In actual electrolysis the yield may be less than that deduced from Faraday's Law, *e.g.*, as a result of secondary changes giving rise to other products of decomposition. The ratio

$$\frac{\textit{actual yield}}{\textit{calculated yield}}$$

is known as the CURRENT-EFFICIENCY of the process, and may reach 100 per

* If E and Q vary with temperature, then instead of $E = Q$ or $E - Q = 0$ we must write

$$E - Q = T\frac{dE}{dT},$$

where T is the temperature measured from − 273°.

cent., *e.g.*, in the silver voltameter. On the other hand, if a high voltage is used in order to overcome the electrical resistance of the cell in which the electrolysis is carried out, the consumption of energy may be excessive even when the current efficiency is high. The ratio

$$\frac{\textit{energy calculated}}{\textit{energy used}} = \frac{\textit{volts (calc.)} \times \textit{amps. (calc.)}}{\textit{volts (used)} \times \textit{amps. (used)}}$$

is called the ENERGY-EFFICIENCY of the process, and may easily be as low as 50 per cent., even when the current efficiency is as high as 95 per cent., since a high voltage is usually needed to secure a large output from the plant.

Electric Batteries.

(*a*) *The Single-fluid Cell.*—In an ELECTRIC BATTERY a chemical change which *liberates* energy is made to take place in such a way that the energy is given out as an electric current instead of as heat or light. In the SINGLE-FLUID CELL, which consists of a plate of zinc and one of platinum dipping into dilute sulphuric acid (compare Fig. 76, where, however, the zinc and platinum are separated by a porous pot containing nitric acid), the chemical action is expressed by the equation

$$Zn + H_2SO_4, aq. = ZnSO_4, aq. + H_2,$$

and the voltage produced is about 0·7.

The electric current passing through the dilute sulphuric acid decomposes it into its radicals as follows:

$$H_2SO_4 = 2H + SO_4.$$

The hydrogen is liberated at the platinum plate or POSITIVE POLE, where the current leaves the battery and from which a flow of positive electricity is obtained when the two poles are joined by a conductor. The SO_4, or sulphate radical, is carried to the zinc plate or NEGATIVE POLE, where the current returns to the battery; it there attacks the zinc and converts it into zinc sulphate,

$$Zn + SO_4 = ZnSO_4.$$

Since this combination liberates more energy than the decomposition of the acid, there is a balance of energy which can be drawn upon for doing work outside the battery.

(*b*) *Polarisation.*—The hydrogen liberated at the platinum plate of a single-fluid cell sets up a resistance and a counter-electromotive force which soon begin to obstruct the passage of the current; this obstruction of the current is known as POLARISATION of the cell. It can be overcome by means of a DEPOLARISER, which gets rid of the hydrogen, usually by oxidising it to water; polarisation then ceases and the electromotive force of the cell is actually increased by the additional energy derived from the oxidation of the hydrogen.

(i) In the GROVE CELL (Fig. 76) the platinum plate is enclosed in a porous pot containing fuming nitric acid; this oxidises the hydrogen to water and increases the *E.M.F.* to 1·8—1·96 volts. The BUNSEN CELL (Fig. 77) differs

from the Grove cell only in that the platinum plates are replaced by blocks of hard conducting GAS CARBON from coal-gas retorts (p. 465).

(ii) The DICHROMATE CELL (Fig. 78), in which oxidation is effected by adding potassium or sodium dichromate (p. 742) to the sulphuric acid of a simple zinc-carbon cell, has an *E.M.F.* of about 2 volts. In the figure the zinc plate is shown between two carbon plates, and arranged so that it can be lifted out of the acid when the cell is not in use.

(iii) In the LECLANCHÉ CELL (Fig. 79) the positive pole is a block of carbon enclosed in a porous pot and surrounded by manganese dioxide (p. 755) which supplies the oxygen required for depolarisation; the negative pole is a zinc rod, but the electrolyte is sal-ammoniac or ammonium chloride, NH_4Cl, instead of sulphuric acid. Depolarisation is slow, but the cell is very suitable for giving intermittent currents, *e.g.*, for electric bells. Its *E.M.F.* is usually about 1·3 volts. The ordinary "dry cell" is of similar construction but with the electrolyte soaked up in some porous material.

(c) Standard Cells.—In the DANIELL CELL (Fig. 80) the positive pole is a copper can containing a saturated solution of copper sulphate;

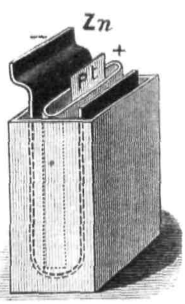


FIG. 76.—GROVE CELL.

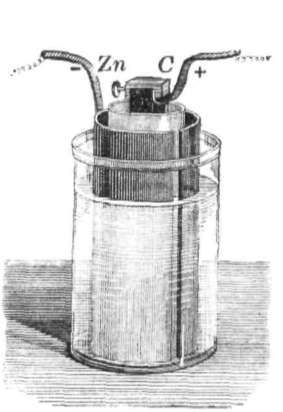


FIG. 77.—BUNSEN CELL.

FIG. 78.—DICHROMATE CELL.

the current therefore deposits copper instead of hydrogen at the positive pole, where the current leaves the cell. The complete action is a precipitation of copper by means of zinc as represented by the equation

$$Zn + CuSO_4 = Cu + ZnSO_4,$$

and this action is not affected if the sulphuric acid surrounding the zinc or negative pole is replaced by a solution of zinc sulphate. The *E.M.F.* of the cell varies with the concentration of the two electrolytes. During the passage of the current the zinc sulphate tends to increase and the copper sulphate to decrease in concentration, both changes tending to diminish the electromotive force of the cell; but by using saturated solutions of these salts the composition of the two liquids

can be kept constant, and a very uniform *E.M.F.* of 1·07 volts can be maintained.

In the CLARK CELL (Fig. 81) the copper and copper sulphate of the Daniell cell are replaced by mercury and a paste of mercuric sulphate, $HgSO_4$. The complete action is a precipitation of mercury by zinc,

$$Zn + HgSO_4 = Hg + ZnSO_4.$$

When a saturated solution of zinc sulphate is used as the electrolyte, the *E.M.F.* of the cell is given very accurately by the formula $e = 1{\cdot}434 - 0{\cdot}0013\ (t - 15)$ volts, where t is the temperature in centigrade degrees. This *E.M.F.* is so steady that it has been adopted as a legal standard of electromotive force. For this purpose the cell is constructed of small dimensions and of high internal resistance, so that only very small currents can be obtained from it.

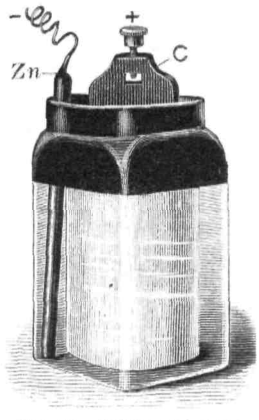


FIG. 79.—LECLANCHÉ CELL.

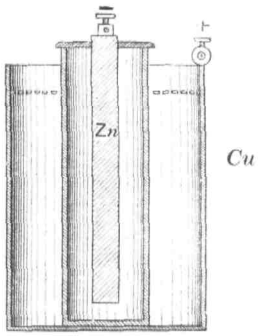


FIG. 80.—DANIELL CELL.

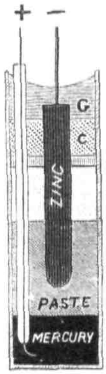


FIG. 81.—CLARK CELL. c = Cork. G = Glue.

In the WESTON CELL (Fig. 82) the zinc and zinc sulphate of the Clark cell are replaced by cadmium (as an amalgam in one limb of an *H*-shaped cell) and cadmium sulphate, so that the complete action is a precipitation of mercury by cadmium :

$$Cd + HgSO_4 = Hg + CdSO_4.$$

This gives an *E.M.F.* of $1{\cdot}019 - 0{\cdot}000038\ (t - 20)$ volts. The Weston cell has the advantages of giving an *E.M.F.* not far removed from 1 volt, and of having a very small temperature coefficient.

(*d*) *Accumulators.*—An electric battery in which the chemical action can be reversed completely by a current passing through it in opposition to its electromotive force is called an ACCUMULATOR. In the LEAD ACCUMULATOR (Fig. 83) the negative and positive electrodes are lead and lead peroxide respectively, mounted in grids of metallic

lead, and the electrolyte is sulphuric acid; the chemical action may be represented by the equation

$$Pb + 2H_2SO_4 + PbO_2 \rightleftharpoons 2PbSO_4 + 2H_2O.$$

The electromotive force increases and decreases with the strength of the acid. When the accumulator is fully charged the density of the acid is about 1·2 and the *E.M.F.* rises to about 2·2 volts; when the *E.M.F.* falls to 1·8 volts the accumulator should be recharged.

In the EDISON ACCUMULATOR the electrodes are iron and nickel peroxide and the electrolyte is a strong solution of potassium hydroxide, which (unlike the sulphuric acid of the lead accumulator) is not liberated or absorbed during charge or discharge, so that the quantity used can be reduced without affecting the capacity of the cell. The chemical actions

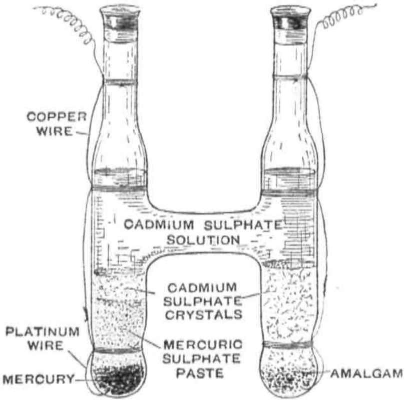


FIG. 82.—WESTON CELL.

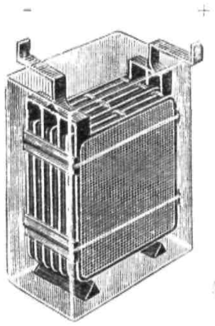


FIG. 83.—LEAD ACCUMULATOR.

which take place during the discharging and charging of the cell may perhaps be represented by the upper and lower arrows in the equation

$$NiO_2 + Fe \rightleftharpoons NiO + FeO.$$

Theory of Electrolytic Dissociation.

According to the theory of electrolytic dissociation put forward by Arrhenius in 1883, a partial decomposition or dissociation of the salt into its ions takes place *as soon as the salt is dissolved in water.* The action is assumed to be a balanced one, *e.g.*,

$$NaCl \rightleftharpoons \overset{+}{Na} + \overset{-}{Cl},$$

but in the case of the majority of salts dissociation into ions is assumed to take place to a very large extent, *e.g.*, 80 or 90 per cent. In the case of strong acids and bases the dissociation is equally extensive, *e.g.*,

$$HCl \rightleftharpoons \overset{+}{H} + \overset{-}{Cl}$$

$$NaOH \rightleftharpoons \overset{+}{Na} + \overset{-}{OH}$$

whilst in weak acids and bases the dissociation is only slight. In the case of water, the dissociation is so slight that the concentration of the ions is only about one equivalent in 10 million litres or, alternatively, only one molecule of water in about 550 million is dissociated into its ions. These conclusions are based on a careful study of the electrical conductivity of aqueous solutions of salts, acids, and bases, on the lines which are set out below.

Equivalent and Molecular Conductivity.

(*a*) The ELECTRICAL CONDUCTIVITY of a salt solution can be measured as the reciprocal of the resistance determined by means of a Wheatstone's bridge; but in order to avoid decomposing the electrolyte (and so setting up at the electrodes the disturbing resistances and electromotive forces known as POLARISATION, p. 195) it is necessary to work with an alternating instead of with a direct current. This alternating current is generally produced by a small induction coil, and the galvanometer of the bridge is usually replaced by a telephone receiver, which is sensitive to alternating currents of suitable frequency, but not to direct currents.

(*b*) The SPECIFIC CONDUCTIVITY of a liquid is defined, in the same way as for solids, as the conductivity between opposite faces of a centimetre cube, and is numerically equal to the current in amperes which would flow between these faces under an electromotive force of one volt. In the case of electrolytes, it can be determined by measuring the conductivity of the liquid in a tube of known length and known diameter, just as has been done in the case of mercury; but it is generally more convenient to measure the conductivity of the solution in a vessel of unknown dimensions and to compare it with that of a standard liquid, the specific conductivity of which has already been determined exactly.

(*c*) The EQUIVALENT CONDUCTIVITY of a solution is the product of its specific conductivity into the volume in cubic centimetres containing one equivalent of the solute; thus, if

K = specific conductivity
Λ = equivalent conductivity
Φ = volume in cubic centimetres containing one equivalent in grams

then $\Lambda = K\Phi$.

The meaning of the equivalent conductivity of a salt can be realised by regarding it as the conductivity which would be observed if one gram-equivalent of the salt were dissolved in water and the whole of the liquid poured into the space between two large vertical electrodes one centimetre apart.

(*d*) Although the specific conductivity decreases rapidly on dilution, the equivalent conductivity is found to increase, that is, the efficiency of the salt as a carrier of the electric current is increased by diluting it with water. This is seen in the following table.

Crystallisation of Mixtures of Salts.

When an aqueous solution containing a pair of salts is evaporated, the least soluble of the four reciprocal salts will separate, *e.g.*, common salt from the mixture already referred to. The balanced action will be disturbed by the separation of this salt, which will continue to separate until the balance is restored by the accumulation in the solution of an excess of the salt associated with it, namely, potassium nitrate.

$$NaNO_3 + KCl \rightleftharpoons \underset{\text{Accumulates in solution}}{KNO_3} + \underset{\text{Precipitated.}}{\mathbf{NaCl}}$$

In this particular case the action from left to right of the equation may be continued by lowering the temperature, when potassium nitrate crystallises out. It is therefore possible by crystallising out common salt at a high temperature and potassium nitrate at a low temperature to secure a complete conversion of sodium nitrate and potassium chloride into potassium nitrate and sodium chloride. This is indeed a commercial method of making potassium nitrate, KNO_3, from Chile saltpetre, $NaNO_3$, and sylvine, KCl.

The concentrations of the four salts may be represented by C_1, C_2, C_3, C_4, where

$$C_1 \times C_2 = K \times C_3 \times C_4.$$

The first effect of evaporation will be to increase all these concentrations equally, until the solution becomes saturated with common salt, when C_4 will become constant. If C_1 and C_2 are then increased by further evaporation, C_3 must increase roughly twice as fast as C_1 and C_2 in order to make up for the fact that C_4 is not increasing at all. This can only be effected by converting sodium nitrate and potassium chloride into potassium nitrate and sodium chloride, which therefore crystallises out continuously from the solution. When the temperature is lowered and potassium nitrate crystallises out, C_3 is also reduced to a constant value determined by the limited solubility of this salt in the cold solution; equilibrium can then be restored only by a diminution of C_1 and C_2, *i.e.*, by a further conversion of sodium nitrate and potassium chloride into potassium nitrate and sodium chloride.

Precipitation of Salts.

From the facts set out above, it follows that if a salt is only sparingly soluble in water, it can be precipitated at once by mixing any pair of salts from which it can be produced by double decomposition. Thus, lead chloride and silver chloride can be precipitated from any soluble salt of lead or silver by the addition of any soluble chloride, *e.g.*,

$$Pb(NO_3)_2 + 2KCl = 2KNO_3 + \mathbf{PbCl_2}$$
$$AgNO_3 + KCl = KNO_3 + \mathbf{AgCl}.$$

This double decomposition is confined to an interchange of the two

radicals into which a salt is resolved by electrolysis. Thus, it is not possible to precipitate silver chloride from a soluble silver salt by means of a chlorate or a perchlorate, since these contain the radicals $-ClO_3$ and $-ClO_4$ and not the simple radical $-Cl$. The precipitation of salts from solution, which is used extensively in qualitative analysis, may be regarded in terms of the theory of electrolytic dissociation as a direct combination of two ions. Thus the precipitation of silver chloride from a soluble silver salt and a soluble chloride may be expressed by the simple "ionic" equation

$$\overset{+}{Ag} + \overset{-}{Cl} = AgCl.$$

According to the Law of Mass Action the dissociation of silver chloride would be controlled by the equation

$$AgCl \rightleftharpoons \overset{+}{Ag} + \overset{-}{Cl}$$
$$K \times C = c_1 \times c_2$$

where K is the DISSOCIATION-CONSTANT of silver chloride, C is the concentration of the undissociated silver chloride, and c_1 and c_2 are the concentrations of the silver and chloride ions in the solution. If only one salt is present so that

$$c_1 = c_2 = c$$

then $$KC = c^2.$$

If α is the coefficient of ionisation and v is the volume containing one gram-molecule of the solute, then $c = \alpha/v$ and $C = (1-\alpha)/v$; the equation $KC = c^2$ can therefore be rewritten $K(1 - \alpha)/v = \alpha^2/v^2$ or $\alpha^2/(1 - \alpha) = Kv$. This relation, which shows the theoretical relationship between the coefficient of ionisation, α, and the dilution, v, is known as Ostwald's DILUTION LAW. It holds good for the electrolytic dissociation of weak acids and bases, but is not accurate for strong acids or bases or for salts.

The slight solubility of silver chloride in water, amounting to about 1·34 mg. per litre, is due almost entirely to its high dissociation at extreme dilutions; it can therefore be diminished very greatly by adding a soluble silver salt or a soluble chloride to drive back the dissociation. Thus, for a saturated solution

$$KC = c_1 \times c_2 = \text{constant},$$

where the constant product $c_1 \times c_2$ is known as the SOLUBILITY PRODUCT of the salt. If c_1 be increased by the addition of a silver salt, c_2 will be reduced proportionally; and if c_2 be increased by the addition of a chloride, c_1 will be reduced. In this way a very complete precipitation of silver can be secured by using an excess of a chloride, or of chloride by using an excess of a silver salt. Concentrated solutions of silver nitrate, of common salt, and of hydrochloric acid, on the other hand, are excellent solvents for silver chloride (p. 850).

Neutralisation.

(*a*) *Strength of Acids and Bases.*—The degree of dissociation of a salt solution, as calculated from its equivalent conductivity, is usually high. In the case of acids and bases, however, the degree of dissociation varies very greatly, the value of α being high in the case of strong acids and bases and low in the case of weak acids and bases. A STRONG ACID or a STRONG BASE is therefore one which has a high coefficient of ionisa-

tion in aqueous solution. This view has been tested by comparing the electrical conductivities of acids and bases with other properties, such as their efficiency in promoting the "inversion" or hydrolysis of sugar, an action which is accelerated very greatly by the addition of acids.

(*b*) *Electrolytic Dissociation of Water.*—In the case of water itself, the coefficient of ionisation is extremely small, the concentration of the ions being only about one equivalent in 10 million litres. When, therefore, an aqueous solution of an acid is mixed with an aqueous solution of a base, the hydrogen ions of the acid will combine with the hydroxyl ions of the base to form water

$$\overset{+}{H} + \overset{-}{OH} = H_2O,$$

and both ions will disappear from the solution almost completely, provided that the acid and base are mixed in equivalent proportions. The neutralisation of an acid by a base may therefore be represented in the following ways.

Ordinary equation.

$$NaOH + HCl = NaCl + H_2O.$$

Ionic equation.

$$\overset{+}{Na} + \overset{-}{OH} + \overset{+}{H} + \overset{-}{Cl} = \overset{+}{Na} + \overset{-}{Cl} + H_2O.$$

It will be seen that in the second equation the sodium and the chlorine ions are assumed to be in the same condition before and after neutralisation; the combination of hydrogen and hydroxyl to form water is therefore independent of the positive radical of the base and of the negative radical of the acid.

(*c*) *Heat of Neutralisation.*—This view finds support in the fact that, when a strong acid is mixed in dilute solution with a strong base, the heat liberated by the neutralisation is practically constant at 13,500 calories per equivalent as shown in the equation

$$\overset{+}{H} + \overset{-}{OH} = H_2O + 13{,}500 \text{ calories}.$$

If, however, the acid or the base is weak, the process of neutralisation will involve a preliminary conversion into its ions of the weak acid, *e.g.* hydrofluoric acid, HF, or of the weak base, *e.g.* ammonium hydroxide, $(NH_4)OH$, and the heat of neutralisation may be greater than the number quoted above, as in the action

$$NaOH + HF = NaF + H_2O,$$

which gives 16,300 calories, or less, as in the action

$$(NH_4)OH + HCl = NH_4Cl + H_2O,$$

which gives 12,200 calories.

(*d*) *Hydrolysis.*—When the acid or the base is weak the phenomena of incomplete neutralisation of the acid and base and of partial

HYDROLYSIS, or decomposition by water (Greek, ὕδωρ, water; λύσις, loosening), of the salt may be observed. Thus, in the action

$$\underset{\text{Potassium hydroxide}}{KOH} + \underset{\text{Hydrogen cyanide}}{HCN} \rightleftarrows \underset{\text{Potassium cyanide}}{KCN} + \underset{\text{Water}}{H_2O} \quad \text{or}$$

$$\overset{+}{K} + \overset{-}{OH} + HCN \rightleftarrows \overset{+}{K} + \overset{-}{CN} + H_2O$$

the degree of dissociation of the prussic acid or hydrogen cyanide, HCN, is only of the same order of magnitude as that of water. The tendency to neutralisation (shown by the upper arrow in the above equations), which depends on the tendency of hydrogen and hydroxyl ions to unite to form water, is therefore partially balanced by the action of hydrolysis, shown by the lower arrow in the equation, since this is assisted by the tendency of hydrogen and cyanogen ions to unite together to form hydrogen cyanide. In this particular case, the proportion of potassium cyanide hydrolysed in a decinormal solution (*i.e.*, in a solution containing one gram-molecule of KCN in 10 litres) at 25° is 1·12 per cent., that is, nearly 99 per cent. of the prussic acid is combined with potash as potassium cyanide, whilst rather more than 1 per cent. remains free. It may be noted that soaps, and other cleansing agents such as washing soda and borax, are all salts in which a strong alkali is combined with a weak acid, so that when the product is dissolved in water it contains a small proportion of free alkali. This free alkali is believed to be responsible, at least in part, for the cleansing action of these substances, perhaps because of the power which the alkalies possess of emulsifying fats and so promoting the removal of greasy dirt.

SUMMARY AND SUPPLEMENT.

1. Faraday's **First Law of Electrolysis** states that

> "*The amount of decomposition is directly proportional to the total current that passes through an electrolyte.*"

Faraday's **Second Law of Electrolysis** states that

> "*When different compounds are decomposed by the same current, equivalent quantities of the various products are obtained.*"

Since the ampere is defined as a current which deposits 1·118 mg. of silver per second, it follows that one gram-equivalent of any compound will be decomposed by the passage of $\frac{107 \cdot 88}{0 \cdot 001118} = 96{,}540$ coulombs of current.

2. **Ions.**—The products of electrolysis are ions or charged radicals carrying 96,540 coulombs per equivalent. The basic or metallic radicals travel with their positive charges as CATIONS to the CATHODE, where the current leaves the electrolyte. The acid or non-metallic radicals travel with their negative charges as ANIONS in the opposite direction to the current, to the ANODE where the current enters.

3. **Primary and Secondary Products.**—When their electrical charges are

given up at the electrodes, the radicals set free by electrolysis may give rise to secondary products as follows :—

(*a*) *Polymerisation.*

(i) $2Cl = Cl_2$
(ii) $2CN = C_2N_2$
(iii) $2HSO_4 = H_2S_2O_8$

(*b*) *Attack on the Anode.*

(i) $NO_3 + Ag = AgNO_3$
(ii) $SO_4 + Cu = CuSO_4$
(iii) $2NO_3 + Pb = Pb(NO_3)_2$

(*c*) *Interaction with the Electrolyte.*

(i) $2Na + 2H_2O = 2NaOH + H_2$
(ii) $2SO_4 + 2H_2O = 2H_2SO_4 + O_2$
(iii) $2NO_3 + Pb(NO_3)_2 = Pb(NO_3)_4$
$Pb(NO_3)_4 + 2H_2O = PbO_2 + 4HNO_3$

4. **Conductivity of Electrolytes.**—The SPECIFIC CONDUCTIVITY of a liquid is the conductivity in reciprocal ohms between opposite faces of a centimetre cube. The EQUIVALENT CONDUCTIVITY of a solution is the product of its specific conductivity into the volume in cubic centimetres containing one equivalent of the solute. The specific conductivity of a solution decreases on dilution, but the equivalent conductivity increases towards a limiting value.

5. **Electrolytic Dissociation.**—The theory of electrolytic dissociation suggests that acids, bases, and salts when dissolved in water are decomposed partially into their ions, *e.g.*,

$$NaCl \rightleftharpoons \overset{+}{Na} + \overset{-}{Cl},$$

and that the DEGREE OF DISSOCIATION or COEFFICIENT OF IONISATION a is given by the ratio Λ/Λ_∞ of the equivalent conductivity Λ to the limiting value Λ_∞ at infinite dilution. In the case of strong acids and bases and of many salts, a degree of dissociation of about 90 per cent. is observed in decinormal solutions ; weak acids and bases give much lower values, *e.g.*, about 1 per cent. for acetic acid and ammonia. The theory of electrolytic dissociation can be used to explain the precipitation of salts, as used in qualitative analysis, and also the various phenomena connected with neutralisation.

6. **Osmotic Pressure of Electrolytes.**—The osmotic pressures of electrolytes are, as a rule, abnormally high, *e.g.*, the molecular depression of the freezing-point in very dilute solutions of potassium chloride is twice as great as that deduced theoretically and twice as great as that observed in the case of cane-sugar. This result can be explained by assuming that each ion of the electrolyte acts as an independent molecule. It is therefore possible to calculate from these measurements the degree of dissociation or coefficient of ionisation of the salt. In very dilute solutions the results agree with those deduced from measurements of electric conductivity, but deviations soon appear when the concentration is increased.

CHAPTER XIX

THE STRUCTURE OF CRYSTALS

The Crystalline and Amorphous States.

It has been shown above (p. 3) that matter may exist in two principal states, namely, the AMORPHOUS STATE, which includes *gases*, *liquids*, and *glassy solids*, and the CRYSTALLINE STATE, which includes solid crystals, both hard and soft, as well as the group of so-called LIQUID CRYSTALS (Figs. 5 and 6) which are so soft that they flow under gravity. The essential difference between these two states is that in the amorphous state the particles are distributed in a chaotic manner, like the individuals in a crowd or the trees in a forest, whilst in the crystalline state they are marshalled in a regular way, like troops on parade or trees in a plantation ; the contrast between the two states is therefore essentially that between chaos and order.

In a crystalline solid the regular marshalling extends without interruption over a limited space, which constitutes the CRYSTAL. This may form a distinct unit, with well-defined flat surfaces, as in the crystals illustrated in Figs. 8, 9, and 10 (p. 11) ; but in a film or in an ingot the boundaries are often irregular, as in Fig. 71 (p. 184) ; the crystalline character of the material is, however, shown by the fact that within that portion of the area of the film, or of the volume of the ingot, which constitutes the crystal, the marshalling of the particles is uniform, whilst in the adjacent areas or volumes the marshalling is similar but oriented in different directions.

Size of Crystals.

The size of a crystal as thus defined may vary very greatly. On the one hand, films of crystalline mica (Fig. 3, p. 4) have been obtained which are only 2 molecules thick ; on the other hand, filaments of plastic tungsten have been prepared (by drawing the filament at such a rate as to enable the particles to marshal themselves as they pass through the die) in which the marshalling is regular throughout the filament, so that the crystal may be a mile or more in length. More usually the size of a crystal, whether natural or artificial, ranges from, say, an inch to perhaps a hundredth of an inch. Minerals such as quartz and felspar are, however, sometimes found in crystals up to about a foot

in diameter, and a few still larger crystals, *e.g.*, of mica and of calcite, have been discovered with a width or thickness of almost a yard ; in one extreme case the dimensions of a natural crystal have extended to 3 feet by 6 feet by 42 feet in length, 37 tons of spodumene having been quarried from a single crystal. Artificial crystals do not reach these extreme dimensions, but crystals of alum and of iron have been prepared with a diameter of more than a foot ; at the other extreme, crystalline structure has been proved to exist in colloidal particles of gold having a diameter of the order of 5 millionths of a millimetre and probably not containing more than 10 atoms in the diameter.

Symmetry of Crystals.

The angles of a crystal are found to be constant within very narrow limits, although the size of the faces may vary greatly. In an ideal crystal, in which all similar faces are equally developed, it is usually possible to recognise in the external form of the crystal the presence of certain ELEMENTS OF SYMMETRY, namely PLANES, AXES, and a CENTRE OF SYMMETRY, as defined below. Since these elements of symmetry are derived from the regular marshalling of the molecules, they must dominate all the physical properties of the crystal as well as its external form.

(i) PLANES OF SYMMETRY divide the crystal into two equal parts in such a way that every perpendicular to the plane intersects the surface of the crystal at equal distances on either side. The idea of a plane of symmetry is well illustrated by the geometrical relationship between an object and its image in a mirror. Some crystals possess no plane and no centre of symmetry ; when reflected in a mirror they show an image of opposite form, which is said to be ENANTIOMORPHOUS (Greek, ἐνάντιος, opposite, μορφή, form), just as a right hand gives a left hand by reflection in a mirror (compare Fig. 92, p. 213).

(ii) AXES OF SYMMETRY are lines about which the crystal can be rotated so as to cover its original position n times during the course of a revolution. Thus a three-bladed propeller is characterised by the presence of a three-fold axis ; and a four-bladed propeller by the presence of a four-fold axis, since the appearance of the propeller is unaltered after rotating through 120° in the first case and 90° in the second. Crystals may show axes of 2-fold, 3-fold, 4-fold, and 6-fold symmetry, but not 5-fold, 7-fold, or 8-fold.

(iii) A CENTRE OF SYMMETRY is a point such that every line drawn through it intersects the surface of the crystal at equal distances on either side. It is impossible for any crystal to possess more than one centre of symmetry, and many crystals do not possess one ; such crystals may be developed in a different way at opposite ends ; they are then classed as HEMIMORPHIC (Greek prefix ἡμι-, half ; μορφή form), and are often PYROELECTRIC, *i.e.*, they develop opposite electrical charges on the ends when heated.

Cubic Symmetry.

Typical elements of symmetry of a simple cube are shown in Fig. 84. Reading from left to right in the figure, these are (i) a *rectangular*

plane of symmetry, parallel to two faces of the cube and dividing each of the other four faces into two rectangles; (ii) a *diagonal plane of symmetry*, passing through two opposite edges of the cube and bisecting two of its faces diagonally; (iii) an *axis of 4-fold symmetry*, passing perpendicularly through the centres of two opposite faces; (iv) an *axis of 3-fold symmetry*, passing through two opposite corners; (v) an *axis of 2-fold symmetry*, passing perpendicularly through the centres of two opposite edges; (vi) a *centre of symmetry* at the mass-centre of the cube.

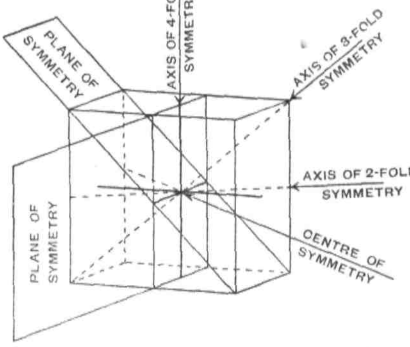


FIG. 84.—ELEMENTS OF SYMMETRY OF THE CUBE.

The elements of symmetry of the cube are 23 in number and include 9 planes, 13 axes, and 1 centre of symmetry as set out in the following table:—

TABLE 27.—ELEMENTS OF SYMMETRY OF THE CUBE.

Planes of symmetry.	
(*a*) Rectangular	3
(*b*) Diagonal	6
Axes of symmetry.	
(*a*) Perpendicular to faces	3- × 4-fold
(*b*) Emerging from corners	4- × 3-fold
(*c*) Perpendicular to edges	6- × 2-fold
Centre of symmetry	1

Identical elements of symmetry are present in the regular octahedron (Fig. 85), but the three axes of 4-fold symmetry emerge from the six corners of the octahedron (as contrasted with the six faces of the cube), whilst the four axes of 3-fold symmetry emerge from the centres of the eight triangular faces of the octahedron (as contrasted with the eight corners of the cube). The cube and octahedron, which possess identical elements of symmetry and may actually appear together as faces of the same crystal, as in Fig. 10 (p. 11), are described as FORMS of the cubic system. Other forms are known in which the number of similar faces is 12, 24, or 48. In each of these forms and in every combination of them the 23 elements of symmetry set out in Table 27 can be recognised.

Holohedral, Hemihedral, and *Tetartohedral Symmetry.*—The striated cube of pyrites (Fig. 86, compare Fig. 36, p. 47) is of a lower order of symmetry than

the simple cube, since the striations destroy both the six diagonal planes of symmetry and the six axes of 2-fold symmetry; they also reduce the three axes of 4-fold symmetry to axes of 2-fold symmetry, since a rotation of 180° instead of 90° is required to bring the striated faces to a position in which they present their original appearance. The system of symmetry seen in the striated cube includes:

3 rectangular planes of symmetry,
4 axes of 3-fold symmetry,
3 ,, 2- ,, ,,
1 centre of symmetry.

It is described as a HEMIHEDRAL SYSTEM OF SYMMETRY (Greek prefix ἡμι-, half; ἕδρα, a seat or base), since the most general form has only 24 faces

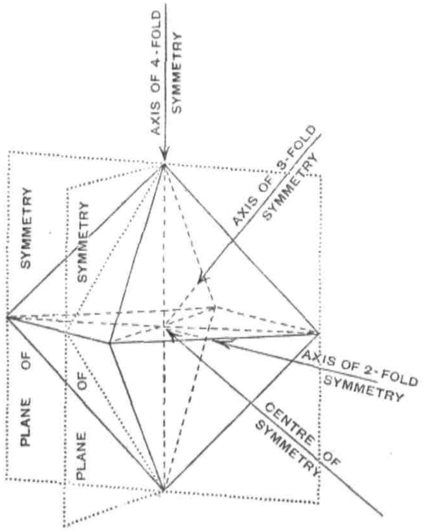


FIG. 85.—ELEMENTS OF SYMMETRY OF THE OCTAHEDRON.

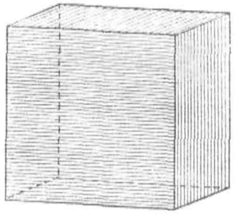


FIG. 86.—STRIATED CUBE OF IRON PYRITES.

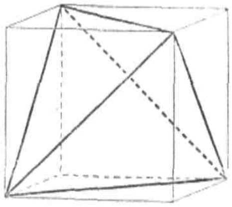


FIG. 87.—TETRAHEDRON AND CUBE.

whereas the complete or HOLOHEDRAL SYMMETRY (Greek ὅλος, whole) of the simple cube gives a general form with 48 faces.

The tetrahedron, a simple figure made up of 4 equilateral triangles, and related very closely to the cube (see Fig. 87), may be regarded as a hemihedral form of the octahedron. Its elements of symmetry are:

6 diagonal planes of symmetry,
4 axes of 3-fold symmetry,
3 ,, 2- ,, ,,

and no centre of symmetry, since there are no pairs of parallel faces. This system of symmetry gives a general form with only 24 faces and is therefore another hemihedral cubic system. There is also a third hemihedral system in which all the axes of the holohedral system are retained, but none of the planes and no centre, and finally a TETARTOHEDRAL SYSTEM (Greek τέταρτος,

one-quarter) with four axes of 3-fold symmetry and three axes of 2-fold symmetry, but without a centre or any planes of symmetry, which gives a general form with 12 instead of 48 faces.

Axes and Systems of Symmetry.

The geometrical form of crystals is usually described by means of the intersections of the faces on three or more CRYSTALLOGRAPHIC AXES. These are selected to coincide as far as possible with the axes of symmetry, and are used to classify crystals into seven SYSTEMS, as follows :—

TABLE 28.—SYSTEMS OF SYMMETRY.

Cubic	3 axes, all equal, all rectangular.
Rhombohedral	3 axes, all equal, all inclined equally.
Tetragonal	3 axes, one unequal, all rectangular.
Orthorhombic	3 axes, all unequal, all rectangular.
Monosymmetric	3 axes, all unequal, one pair inclined.
Anorthic	3 axes, all unequal, all inclined.
Hexagonal	4 axes, three equal at 60°, the fourth unequal (compare tetragonal system) and rectangular.

Under these seven systems of axes there are grouped 32 main systems of symmetry or 230 subordinate systems.

The *cubic system* includes the elements P, Si, Fe, Cu, Pb, Hg, Ag, Au, Pt with carbon in the form of diamond (Fig. 176, p. 445); rock salt, NaCl (Fig. 33, p. 45), and fluorspar, CaF_2 (Fig. 235, p. 633); galena, PbS (Fig. 10,

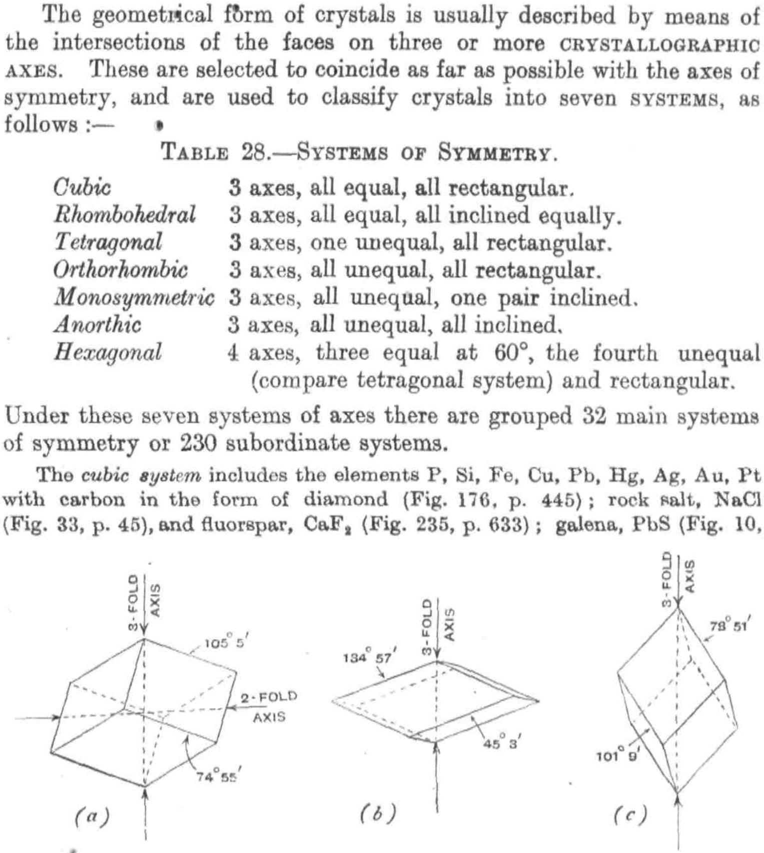


FIG. 88.—RHOMBOHEDRAL CRYSTALS OF CALCITE.

(*a*) is identical with the rhombohedra produced by cleavage. (*b*) is a secondary rhombohedron produced by truncating the edges of (*a*). (*c*) is a rhombohedron which gives rise to (*a*) when its edges are truncated.

p. 11), argentite, Ag_2S, and iron pyrites, FeS_2 (Fig. 36, p. 47); the alums (Figs. 8 and 9, p. 11); magnetite, Fe_3O_4 (Fig. 267, p. 781), and the spinels such as $MgAl_2O_4$; with garnet (Fig. 227, p. 623) and leucite amongst the silicates.

The *rhombohedral system* (the holohedral form of which has three planes and a centre of symmetry in addition to one 3-fold and three 2-fold axes, compare Fig. 88*a*) includes the elements arsenic, antimony, and bismuth; the "metallic" forms of phosphorus, selenium and tellurium; ice; calcite, $CaCO_3$ (Fig. 88), and the isomorphous carbonates, magnesite, $MgCO_3$, calamine,

$ZnCO_3$, and siderite, $FeCO_3$, with sodium nitrate, $NaNO_3$; and tourmaline amongst the silicates.

The *tetragonal system*, with a single axis of 4-fold symmetry as its chief characteristic, includes boron and tin; cassiterite, SnO_2 (Fig. 89), rutile and anatase, TiO_2, and zircon, $ZrSiO_4$.

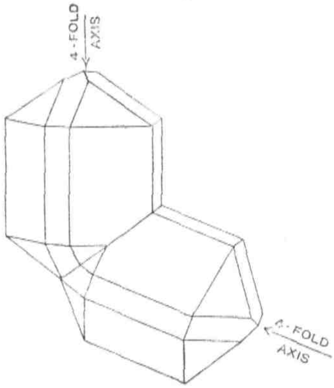
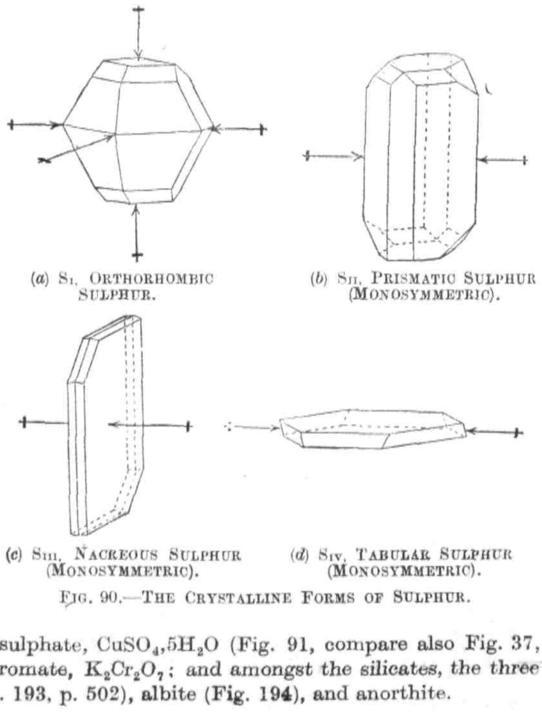


FIG. 89.—TETRAGONAL CRYSTALS OF CASSITERITE (TWINNED).

The *orthorhombic system*, the holohedral form of which has 3 planes and 3 axes of symmetry at right angles to one another, includes iodine and the common form of sulphur (Fig. 90*a*); the common forms of potassium and silver nitrates; calcium carbonate in the form of aragonite (Fig. 233, p. 630), with the isomorphous carbonates, witherite, $BaCO_3$, and cerussite, $PbCO_3$; barytes, $BaSO_4$ (Fig. 239, p. 647), with the isomorphous sulphates, celestine, $SrSO_4$, and anglesite, $PbSO_4$; anhydrite, $CaSO_4$; potassium sulphate, K_2SO_4, and the isomorphous chromate, K_2CrO_4; and olivine (Fig. 198, p. 509), Fe_2SiO_4 with Mg_2SiO_4, and topaz, $(AlF_2)AlSiO_4$ (Fig. 201, p. 514), amongst the silicates.

The *monosymmetric system* (also called monoclinic) includes the three less stable forms of sulphur which are shown (with a single axis and plane of symmetry at right angles to one another) in Fig. 90 (*b*), (*c*), and (*d*); the double sulphates of the series $K_2Mg(SO_4)_2,6H_2O$; gypsum, $CaSO_4,2H_2O$ (Fig. 38, p. 49); and amongst the silicates orthoclase, mica (Fig. 196, p. 505, and Fig. 197, p. 506), augite (Fig. 199), and hornblende.



(*a*) S_I, ORTHORHOMBIC SULPHUR. (*b*) S_{II}, PRISMATIC SULPHUR (MONOSYMMETRIC). (*c*) S_{III}, NACREOUS SULPHUR (MONOSYMMETRIC). (*d*) S_{IV}, TABULAR SULPHUR (MONOSYMMETRIC).

FIG. 90.—THE CRYSTALLINE FORMS OF SULPHUR.

The *anorthic system* (also called triclinic), which has no axes and no planes of symmetry but which usually has a centre of symmetry and therefore parallel faces, includes copper sulphate, $CuSO_4,5H_2O$ (Fig. 91, compare also Fig. 37, p. 47); potassium dichromate, $K_2Cr_2O_7$; and amongst the silicates, the three felspars microcline (Fig. 193, p. 502), albite (Fig. 194), and anorthite.

The *hexagonal system*, which has a single 6-fold axis, often reduced to a 3-fold axis in hemihedral and tetartohedral forms, includes the elements

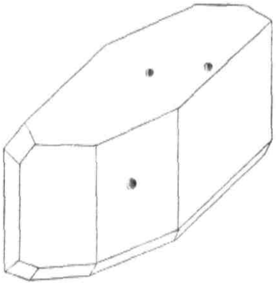
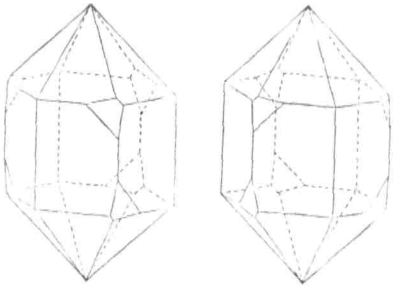


FIG. 91.—ASYMMETRIC CRYSTAL OF COPPER SULPHATE.



(*a*) Right-handed. (*b*) Left-handed.

FIG. 92.—HEXAGONAL CRYSTALS OF QUARTZ.

These crystals have one vertical axis of 3-fold symmetry and three horizontal axes of 2-fold symmetry, but they have no planes and no centre of symmetry. Two enantiomorphous forms of the crystal are shown, which are "mirror-images" of one another.

Be, Mg, Zn, Cd, with carbon in the form of graphite; cinnabar, HgS; quartz, SiO_2 (Fig. 92); with beryl and nephelite amongst the silicates.

Crystalline Structure of Elements.

In the case of an element with a monatomic molecule, it is possible to picture the crystal as an aggregate of atoms arranged in a regular manner, without stopping to consider the structure of the atom or the more remote question of whether the atoms themselves are all oriented in the same way or indeed are sufficiently in repose for this phrase to have any meaning. For this purpose it is convenient to assign to each atom a *sphere of influence*, and to consider how these spheres may be packed together.

(*a*) *Cubic Symmetry.*—The close-packing of spheres in a plane gives rise to the triangular pattern shown by heavy circles in Fig. 93, but from these triangular layers it is easy to build up a cube, *e.g.*, as in Fig. 94, where the missing corner in (*a*) can be filled in as in (*b*) by adding to the triangle of $5+4+3+2+1=15$ spheres a triangular layer containing $3+2+1=6$ spheres, and finally a single sphere to complete the corner of the cube. This last sphere lies above a hollow in the second and third layers, but is immediately opposite to a sphere in the fourth layer below it, which would correspond exactly with the first if this were extended to the same extent; these successive layers are shown

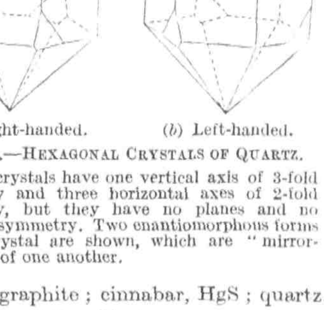
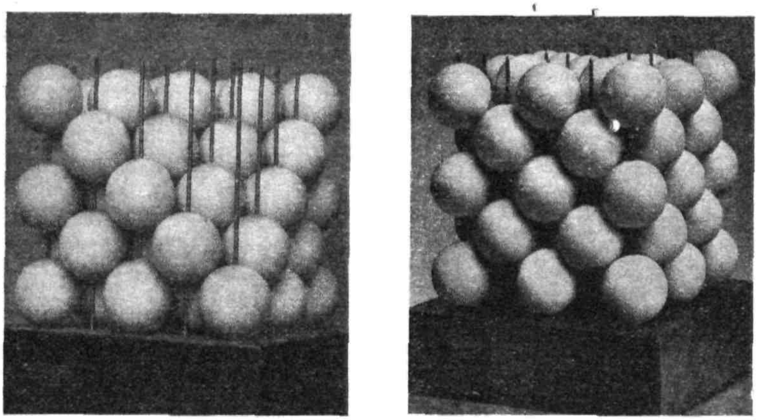


FIG. 93.—CLOSE-PACKING OF SPHERES.

in Fig. 93 by (i) broken circles, (ii) thin-line circles, (iii) thick-line circles. The same type of marshalling may equally give rise to a regular octahedron (Fig. 95), or to any other figure having the same symmetry as the cube, by extending the various layers to a



(a) (b)

FIG 94.—CUBE BUILT UP FROM CLOSE-PACKED SPHERES.

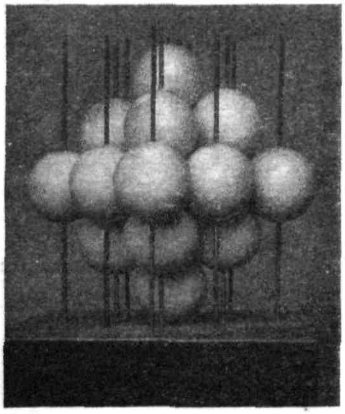


FIG. 95.—OCTAHEDRON BUILT UP FROM CLOSE-PACKED SPHERES.

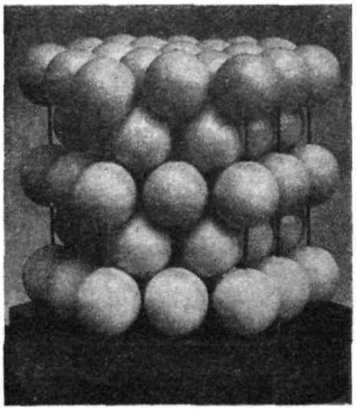


FIG. 96.—HEXAGONAL PRISM BUILT UP FROM CLOSE-PACKED SPHERES.

different extent. This type of symmetry and method of marshalling are actually observed in the crystals of many of the elements, including aluminium; lead; copper, silver, and gold; cobalt (one form) and nickel; rhodium and iridium, palladium and platinum.

(*b*) *Hexagonal Symmetry.*—On referring again to Fig. 94 (*a*) it will be seen that the exposed triangle of spheres could be covered equally well by a triangle containing $4 + 3 + 2 + 1 = 10$ spheres, followed by $3 + 2 + 1 = 6$ spheres, $2 + 1 = 3$ spheres, and finally 1 sphere; but this would make the corner much too sharp for a cube. This alternative arrangement of the layers of spheres gives rise to the structure shown in Fig. 96, where, however, the layers are shown as hexagonal in outline, instead of triangular, and are retained in a horizontal position, instead of being tilted as in Fig. 94. In this arrangement, the third layer is immediately above the first, the fourth above the second, etc. The new model has the symmetry of a hexagonal prism, but may be tapered at each end to form a hexagonal pyramid. This type of symmetry and method of marshalling are found in

beryllium, magnesium, zinc, and cadmium (mercury is cubic),

but the agreement between the observed axial ratios and those deduced from the model is not very close except in the case of magnesium. Arsenic, antimony, bismuth, and tellurium, although also hexagonal, are marshalled differently.

Crystalline Structure of Compounds.

This involves more complex considerations than in the case of elements, since there is very clear evidence to show that the atoms of a compound are arranged in a definite manner in the molecule, giving rise amongst other effects to the phenomenon of isomerism (p. 321), when two different arrangements of the atoms are possible. It is therefore necessary in discussing the crystalline structure of compounds to consider not merely the marshalling of the molecules in the crystal, but also the marshalling of the atoms in the molecule. In this connection the idea of the SPACE-LATTICE has proved most useful.

This conception may be illustrated by considering its application to the pattern on a flowered wall-paper, where a lattice of horizontal, vertical, and diagonal lines may be drawn through any unit of the pattern, *e.g.*, a rosebud, in such a way that this unit appears at regular intervals along each line. It will then be found that the same lattice can be made to cover any other unit of the pattern merely by moving it parallel to itself. In the same way, if a space-lattice in three dimensions be drawn through the atoms of lead in a crystal of galena, PbS, the atoms of sulphur should be located at the intersections of the lines of a parallel lattice.

Diffraction Spectra and X-ray Spectra.

In optics DIFFRACTION-SPECTRA are produced by transmitting or reflecting light at a surface closely and uniformly ruled with a large number of equidistant parallel lines, separated by a distance of perhaps 1/10,000 inch from one another, or say 400 lines to the millimetre. The deviation θ of the diffracted ray is given by the equation

$$d \sin \theta = n\lambda,$$

where d is the distance between the parallel lines, λ is the wave-length of the light, and n is a small integer giving the "order" of the spectrum, namely, 1 for the spectrum of the first order (the least diffracted and the strongest in intensity) and 2, 3, 4, etc., for successive spectra. By means of this equation, when the deviation of a ray has been measured, its wave-length can be calculated from the distance between the rulings of the grating or conversely.

It is now known that X-rays are identical with light, but of wave-length about 10,000 times smaller, *e.g.*, the sodium flame gives a pair of yellow lines of wave-lengths

$$5890 \text{ and } 5896 \times 10^{-8} \text{ cm. or } 5890 \text{ to } 5896 \text{ Ångström units,}$$

whilst an X-ray tube with a palladium anticathode (p. 541) gives a ray of wave-length 0·521 and a doublet of wave-lengths

$$0{\cdot}586 \text{ and } 0{\cdot}590 \times 10^{-8} \text{ cm. or } 0{\cdot}586 \text{ and } 0{\cdot}590 \text{ Ångström units.}$$

The equally-spaced planes of atoms forming the space-lattice of a crystal have been found to act as diffraction gratings for X-rays, their distances being comparable with the Ångström unit just as the rulings of a grating (*e.g.*, 25,000 cm.$^{-8}$ or Å.U.) are comparable with, but usually much greater than, the wave-lengths of visible light. If the distance d between the planes of atoms in a crystal is known, the wave-length of the X-rays diffracted from it can be calculated by means of the formula $n\lambda = 2d \sin\theta$, where θ is the glancing angle at which the rays fall on the reflecting planes; and conversely, by employing X-rays of known wave-length the distances between the successive planes of atoms in a crystal can be deduced from the deviation of the ray.

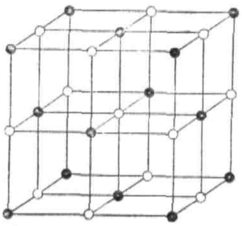


FIG. 97.—SPACE-LATTICE FOR COMMON SALT.

Assuming that the atoms of sodium and chlorine occupy the positions shown by the black and white dots in Fig. 97, the distances between the planes can be calculated as follows:

Molecular weight of sodium chloride $= 23 + 35{\cdot}5 = 58{\cdot}5$.
Number of molecules in 1 gram-molecule, *e.g.* 58·5 grams of salt, $= 60{\cdot}62 \times 10^{22}$.
Weight of 1 c.c. of salt $= 2{\cdot}17$ grams.

Number of molecules in 1 c.c. of salt $= \dfrac{2{\cdot}17}{58{\cdot}5} \times 60{\cdot}62 \times 10^{22} = 2{\cdot}26 \times 10^{22}$.

Number of atoms in 1 c.c. of salt $= 4{\cdot}52 \times 10^{22}$.

The volume allotted to each atom is the reciprocal of this number $= 0{\cdot}221 \times 10^{-22}$ c.c. or $22{\cdot}1 \times 10^{-24}$ c.c., and the distance between the atoms is the cube root of this or $\mathbf{2{\cdot}81 \times 10^{-8}}$ cm. When the distance between the atoms in common salt is thus known, diffraction from a salt crystal can be used to establish the wave-length of X-rays, *e.g.*, from a palladium or a rhodium anticathode; these rays can then be used to determine the distances between the planes in other crystals.

Crystalline Structure of Elements and Compounds.

Some examples of the crystalline structure of elements and compounds as determined by W. H. and W. L. Bragg by examination with X-rays are set out below.

(*a*) *Sodium Chloride and Potassium Chloride.*—The space-lattice for the cubic crystals of sodium chloride is shown in Fig. 97. A model in which the atoms of sodium and of chlorine are represented by large and small spheres is shown in Fig. 98(*a*). A precisely similar model* may

FIG. 98(*a*).—COMMON SALT.

FIG. 98(*b*).—CALCITE.

be used to represent potassium chloride, KCl, magnesium oxide, MgO, lead sulphide, PbS, and many other binary compounds crystallising in the cubic system.

In all these models each atom of metal is surrounded by six atoms of non-metal and conversely; there is, however, no evidence that the atom of metal is attached specifically to any of the six atoms of non-metal, or conversely; it has therefore been suggested that the crystal is built up not from molecules but from ions, similar to those which are postulated in aqueous solutions of the salt. The ATOMIC RADII (compare Fig. 210, p. 548), which express the distances between the atoms in these crystals, as deduced from X-ray examination by W. L. Bragg, are given below in Ångström units (10^{-8} cm.), identical with those used in measuring the wave-length of light.

Sodium	1·77	Chlorine	1·05
Potassium..	2·07	Oxygen	0·65
Magnesium	1·42	Sulphur	1·02
Lead	1·90		

(*b*) *Calcite.*—The corresponding model for calcite, $CaCO_3$, is shown in Fig. 98(*b*), where the large spheres represent calcium and the clusters of one small black and three small white spheres represent the carbonate radical, CO_3. These clusters occupy positions corresponding with those of the chlorine atoms in the cube of rock salt, Fig. 98(*a*), but the cube is here distorted to a rhombohedron as if by compression between two opposite corners. The successive layers from which the rhombohedron

* Some modification of this model is needed to express the fact that both sodium and potassium chloride give crystals of lower symmetry than the simple cube.

is built up are shown in Fig. 99. Many other salts containing a compound instead of a simple negative radical can be represented by a similar model.

(c) *Iron Pyrites.*—The striated cubes of iron pyrites, which are of a

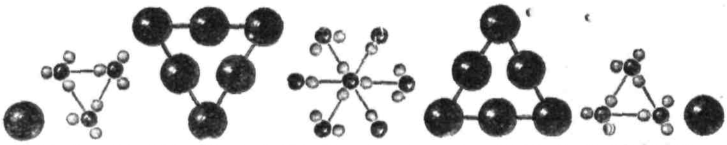


FIG. 99.—CALCITE. Showing successive layers used to build up the rhombohedron.

lower symmetry than the simple cube, are represented by the model shown in Fig. 100, where the atoms of iron are represented by black spheres and the atoms of sulphur by white spheres. In the complete lattice the white spheres are twice as numerous as the black, since the black spheres shown in the figure are shared with adjacent cells of the space-lattice. When the small spheres of Fig. 100 are expanded until they touch, to correspond with the other cubic models, their diameters are in agreement with the atomic radii.

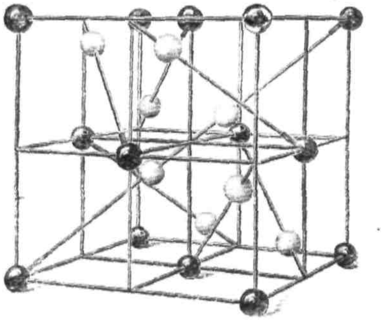
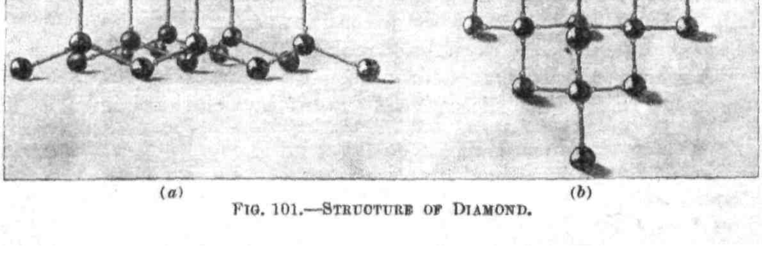


FIG. 100.—IRON PYRITES.

Iron $= 1{\cdot}40 \times 10^{-8}$ cm.
Sulphur $= 1{\cdot}02 \times 10^{-8}$ cm.

(d) *Diamond.*—The arrangement of the atoms in the diamond is shown in Fig. 101. Each atom is surrounded by four others, and if



(a) (b)

FIG. 101.—STRUCTURE OF DIAMOND.

the small spheres of the model were expanded until they came in contact each sphere would touch the four spheres surrounding it. These four surrounding atoms occupy the corners of a tetrahedron, with the first atom at its mass-centre ; this arrangement agrees exactly with that which chemists have assigned to the five atoms in the molecule of methane, CH_4, where the four hydrogen atoms are placed at the corners of a tetrahedron with the carbon atom at its centre. Unlike the models of the metallic compounds described under (*a*), (*b*), and (*c*) above, the diamond model displays the recognised valency of the carbon atom.

The model reproduced in Fig. 100(*a*) shows a series of layers of atoms the distances between which, as tested by X-ray analysis, are in the ratios 1 : 3 : 1 : 3 etc. The model as a whole is a tetrahedron or regular triangular pyramid, and presents the same appearance on whichever of the four triangular faces it rests. As indicated in Fig. 87, the tetrahedron is related very closely to the cube, and by tilting the model as in Fig. 101(*b*) the rectangular outline of the cube can be clearly shown ; the rows of atoms are, however, parallel to the diagonals of the cube and not to its edges. This model corresponds with a holohedral symmetry of the crystals, although the octahedron, which is the commonest form of the diamond, as seen in Fig. 176 (p. 445), is generally held to be a combination of two tetrahedra, and therefore hemihedral.

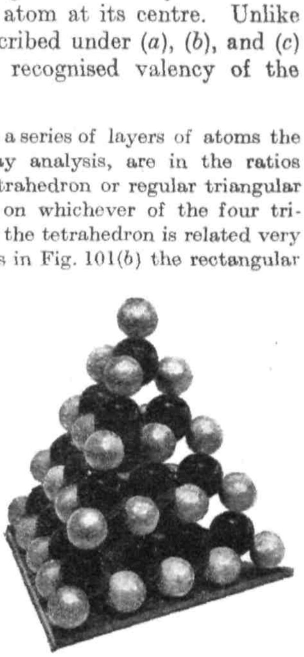


FIG. 102.—ZINC BLENDE (cubic)

(*e*) *Zinc Sulphide and Aluminium Oxide.* — Zinc sulphide is dimorphous, occurring in cubic crystals as blende, and in hexagonal crystals as wurtzite. The cubic crystals of blende are represented by the model shown in Fig. 102.

The structure of this model may be compared with that of the diamond : thus an examination of Fig. 101(*a*) shows the presence in the diamond of vertical pairs of atoms packed into a triangular pattern ; one such pair of atoms is seen at the top of the model, below it are triangles containing 3 and 6 pairs of atoms. In blende these vertical pairs of similar atoms are replaced by pairs of dissimilar atoms, as shown in Fig. 102, where

Black	= zinc,	atomic radius	$1{\cdot}32 \times 10^{-8}$ cm.
White	= sulphur,	atomic radius	$1{\cdot}02 \times 10^{-8}$ cm.

In this model each black sphere is surrounded symmetrically by 4 white spheres, and conversely, and the model exhibits a hemihedral cubic type of symmetry. The hexagonal crystals of wurtzite may be derived from Fig. 96 by substituting a vertical pair of black and white spheres for each sphere in the model.

The structure of alumina is shown in Fig. 103, where the unit, Al_2O_3, con-

sists of two large spheres, *A A*, representing the metallic atoms, with three smaller spheres, *B B B*, representing the oxygen atoms, clustering round them; the triangular packing of these units gives rise only to rhombohedral symmetry.

SUMMARY AND SUPPLEMENT.

1. *Structure of Crystals.*—Crystals are characterised by a regular marshalling of the atoms, which are distributed on a series of inter-penetrating SPACE-LATTICES in such a way that each similar point in the crystal has an identical environment. The constants of these lattices can be determined by examination with X-rays, which are reflected and diffracted by the layers of atoms of which the crystal is composed. It is then possible to represent the structure of the crystal by an aggregate of spheres, each representing the sphere of influence of an atom. The ATOMIC RADII of these spheres, as deduced by W. L. Bragg, for a large number of the elements are given in Table 64, p. 548.

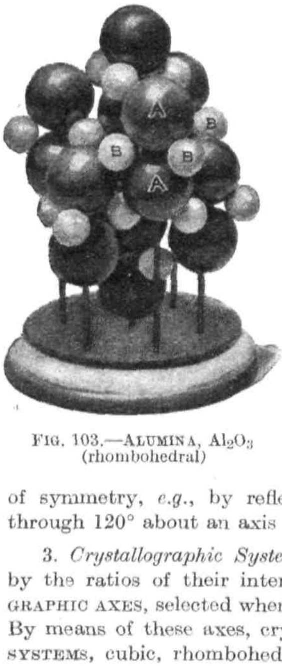


FIG. 103.—ALUMINA, Al_2O_3 (rhombohedral)

2. *Symmetry of Crystals.* — The exterior surface of a well-formed crystal is composed of plane-surfaces, which may vary in size but intersect at constant angles. In an ideal crystal, in which all similar faces are equally developed, it is possible to detect (i) PLANES OF SYMMETRY, (ii) AXES of 2-, 3-, 4-, or 6-fold symmetry, (iii) a CENTRE OF SYMMETRY. These ELEMENTS OF SYMMETRY are used in classifying crystals in a series of thirty-two systems of symmetry. The similar faces of a crystalline FORM (cube, octahedron, prism, etc.) can be developed from a single face by making use of the elements of symmetry, *e.g.*, by reflection across the planes of symmetry, rotation through 120° about an axis of 3-fold symmetry, etc.

3. *Crystallographic Systems.*—The faces of a crystal are usually located by the ratios of their intercepts on three (or sometimes four) CRYSTALLOGRAPHIC AXES, selected when convenient from amongst the axes of symmetry. By means of these axes, crystals are grouped into seven CRYSTALLOGRAPHIC SYSTEMS, cubic, rhombohedral, tetragonal, hexagonal, orthorhombic, monosymmetric, and anorthic. Each crystallographic system includes several systems of symmetry, which are distinguished as HOLOHEDRAL, HEMIHEDRAL, and TETARTOHEDRAL, according to the number of faces in the general form.

4. *Simple Lattices.*—The simple CUBIC LATTICE (Fig. 97) is common in binary compounds, rare amongst elements. Some metals (Fe, Cr, Ti, Ta, W) crystallise on a CENTRED CUBIC LATTICE, with atoms at the corners and mass-centres of the cubes. Others (Cu, Ag, Au, etc., p. 214) crystallise on a FACE-CENTRED CUBIC LATTICE, with an atom (or ion) at the corners and at the centre of each face of the cubes (and perhaps an electron replacing each halogen atom in Fig. 97). Other elements and compounds are built on a HEXAGONAL LATTICE (compare Fig. 96).

INORGANIC CHEMISTRY

PART II.—NON-METALS

CHAPTER XX

1. HYDROGEN.* H = 1·008.

Occurrence of Hydrogen.

Traces of hydrogen (about 1 part per million) are found in a free state in the atmosphere. In combination with oxygen, hydrogen forms one-ninth part by weight of water, of which 2 per cent. is present in the solid crust of the earth (mainly in combination with silica in deep-seated igneous rocks), whilst the ocean contains about 96½ per cent. of water. Hydrogen is also found in combination with carbon in mineral oils (petroleum, etc.) and is present, in combination with carbon, oxygen, and other elements, in almost all organic materials, including oils, fats, wood, peat, coal, etc. The outer ten miles of the earth's crust, including the ocean and the atmosphere, contain about 1 per cent. of hydrogen, as contrasted with 50 per cent. of oxygen.

Preparation of Hydrogen.

(*a*) *By the action of Metals on Acids, e.g.*,

$$Zn + H_2SO_4 = \underset{\text{Zinc sulphate}}{ZnSO_4} + H_2$$

$$Sn + 2HCl = \underset{\text{Stannous chloride}}{SnCl_2} + H_2.$$

The metals which liberate hydrogen from dilute acids include magnesium, aluminium, zinc, iron, and tin. Copper, silver, and mercury will dissolve in oxidising acids, such as strong sulphuric acid or dilute nitric acid, but they do not liberate hydrogen, the sulphuric acid being reduced to sulphur dioxide and the nitric acid to oxides of nitrogen instead. Gold and platinum are usually dissolved in chlorinating acids such as aqua regia, when chlorides are formed by direct combination of the metal with chlorine.

* The name of the element is preceded by its serial or atomic number (p. 535) and followed by its symbol and atomic weight.

In the laboratory hydrogen is commonly prepared from zinc and sulphuric acid (Fig. 104); the product contains arseniuretted hydrogen (removed by silver sulphate), sulphuretted hydrogen (removed by lead nitrate), and sulphur dioxide (removed by alkalies, compare Chapter VIII, Fig. 47, p. 89). The action of zinc on sulphuric acid depends on the presence of impurities, since highly purified zinc does not dissolve in dilute sulphuric acid. The action can also be checked by amalgamating the zinc, which has the same effect as purifying it; conversely, when the zinc is coated with finely-divided copper, it becomes much more active, and the ZINC-COPPER COUPLE produced in this way will decompose boiling water. The presence of water is necessary in all these actions, since pure anhydrous acids have little or no action on metals.

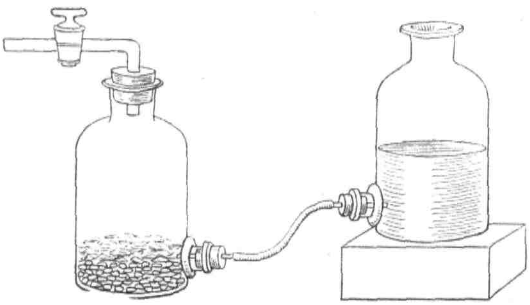


FIG. 104.—APPARATUS FOR PREPARATION OF HYDROGEN FROM ZINC AND SULPHURIC ACID.

Molten zinc is poured out to form a rough plate, which is broken into fragments small enough to pass through the neck of the bottle. These fragments rest upon a layer of marbles or pebbles. When the tap is turned off the acid is driven back into the second bottle and drains away from the zinc.

(*b*) *By the action of Metals on Alkalies, e.g.*,

$$Zn + 2NaOH = Na_2ZnO_2 + H_2.$$
odium zincate

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2.$$
Sodium aluminate

$$FeSi + 2NaOH + H_2O = Fe + Na_2SiO_3 + 2H_2.$$
Ferro-silicon; Sodium silicate

The action of 90 per cent. ferrosilicon on sodium hydroxide is used in preparing hydrogen for military service, since the alkali is much more portable than an acid; the heat of dissolution of the soda is sufficient to start the action, which then proceeds very energetically.

(*c*) *By the action of Metals on Water, e.g.*,

(i) $2Na + 2H_2O = 2NaOH + H_2$ or
$2NaHg_2 + 2H_2O = 4Hg + 2NaOH + H_2$.
(ii) $Mg + H_2O = MgO + H_2$ or
$Mg + 2H_2O = Mg(OH)_2 + H_2$.
(iii) $Zn + H_2O = ZnO + H_2$ or
$Zn + 2H_2O = Zn(OH)_2 + H_2$.
(iv) $3Fe + 4H_2O = Fe_3O_4 + 4H_2$.

(i) Sodium decomposes water very vigorously, but pure hydrogen can be prepared by the action of the metal on water-vapour. The violence of the action can also be checked by using sodium amalgam (containing compounds such as $NaHg_2$), instead of the free metal; aluminium amalgam, on the other hand, will decompose water readily although the metal in its ordinary form shows no marked interaction with water.

(ii) Magnesium takes fire and burns when heated in a current of steam; magnesium amalgam is more active and decomposes cold water quite readily, forming magnesium hydroxide, $Mg(OH)_2$.

(iii) Metallic zinc will decompose steam, and a zinc-copper couple, prepared by immersing the metal in a solution of copper sulphate, will decompose boiling water.

(iv) The decomposition of steam by iron, unlike the preceding actions, is reversible (pp. 87 and 94), proceeding in one direction or the other according as water-vapour or hydrogen is in excess. In preparing hydrogen by this process, the oxide of iron is alternately reduced to metal by means of "water-gas" (see (*d*) below) during a period of twenty minutes and oxidised by steam during a period of ten minutes at a constant temperature of 650°.

(*d*) *By the action of Carbon on Steam.*

$$C + H_2O = CO + H_2.$$

The mixture of carbon monoxide and hydrogen produced in this way is known as WATER-GAS (p. 468). Pure hydrogen may be prepared from it on a commercial scale by cooling to − 200° by liquid air boiling under reduced pressure and so freezing out the carbon monoxide and all other impurities; where a less pure product is required, the carbon monoxide can be decomposed by steam in presence of a catalyst at 400° (p. 470), giving rise to a second molecule of hydrogen,

$$CO + H_2O = CO_2 + H_2.$$

(*e*) *By Electrolysis, e.g.*,

$$2H_2O = 2H_2 + O_2.$$

Pure water is not a conductor, but becomes so in presence of salts, acids, or alkalies. For preparing hydrogen and oxygen by electrolysis alkalies are preferred, as they give a purer product than when acids are used, *e.g.*, very pure hydrogen and oxygen can be prepared by electrolysing an aqueous solution of barium hydroxide; large quantities of hydrogen are produced commercially as a by-product from the electrolysis of common salt in the manufacture of alkalies and bleach (p. 565).

Physical Properties of Hydrogen.

(*a*) *Gas.*—Hydrogen is a colourless, odourless gas. Its density, 0·0899 gram per litre at 0° and 760 mm. pressure, is less than that of all other gases; it is therefore used for inflating balloons and airships,

either in a pure state or in the form of coal gas ; helium, which is twice as dense as hydrogen but is not inflammable, has been proposed as an alternative, for use especially in war On account of its lightness, hydrogen diffuses more rapidly than any other gas ; thus, in accordance with Graham's LAW OF DIFFUSION (p. 15), which states that "the velocity of diffusion of a gas varies inversely as the square root of the density," oxygen, which is sixteen times heavier than hydrogen, diffuses with only one-fourth the velocity.

Water at 8° dissolves 2 per cent. of its own volume of hydrogen, as compared with 4 per cent. of oxygen and 2 per cent. of nitrogen.

(*b*) *Liquid.*—Hydrogen can be liquefied by cooling it with liquid air and allowing the cold compressed gas to escape from a nozzle ; the gas moving towards the nozzle is cooled by the expanded gas from the nozzle and finally escapes from compression in a liquid form. The apparatus used for this purpose is shown in Fig. 147 (p. 375). Liquid hydrogen boils at − 253° and is a convenient agent to use when extreme cold is required. Only one gas, namely helium boiling at − 270°, is known of lower boiling-point than hydrogen. Hydrogen can therefore be purified from all other gases by cooling it, especially in the presence of charcoal, which, at the temperature of liquid air, will absorb completely all gases except hydrogen, neon, and helium.

Liquid hydrogen is one of the lightest liquids known, its density being only 0·07 as compared with 0·15 for liquid helium and about 0·7 for the lightest organic compound. The difference in density between liquid hydrogen and its vapour is so small that it is difficult to see where the liquid ends and the vapour begins.

(*c*) *Solid.*—By evaporating rapidly under reduced pressure, liquid hydrogen is cooled to such an extent that it freezes to a crystalline solid melting at − 259°. This is the lightest solid known, its density being 0·076 as compared with 0·53 for solid lithium.

(*d*) *Absorption by Metals.*—Hydrogen possesses the property of dissolving in many metals and can therefore pass through metallic membranes. Palladium, which absorbs up to 900 volumes of hydrogen at atmospheric temperatures, but releases it again when heated; can be used for the purification of hydrogen (p. 91). As a consequence of its solubility in metals, hydrogen can diffuse very rapidly through a membrane of palladium, and less rapidly through a membrane of platinum.

Chemical Properties of Hydrogen.

(*a*) *Combination with Oxygen.*—Hydrogen burns in air or oxygen with formation of water,

$$2H_2 + O_2 = 2H_2O.$$

Ignition usually occurs at about 580°, but when a mixture of pure hydrogen and oxygen is carefully dried with phosphoric oxide in a clean tube of hard glass, a silver wire can be melted in it at a temperature of

960° without causing it to explode (compare Fig. 112, p. 245). In the presence of finely-divided platinum or palladium, on the other hand, the combination of hydrogen with oxygen takes place at atmospheric temperatures; but the temperature soon rises to a point at which the mixture inflames. This principle was made use of many years ago in the Doebereiner lamp, in which a jet of hydrogen was ignited by allowing it to impinge on spongy platinum; coal-gas, petrol-vapour, or the vapour of methyl alcohol is inflamed by the same method in some modern gas-lighters and pipe-lighters.

(*b*) *Combination with Halogens.*—Hydrogen and *fluorine* (p. 299) combine violently even at the temperature of solid hydrogen, when all other chemical actions are stopped,

$$H_2 + F_2 = 2HF.$$

Hydrogen and *chlorine* (p. 268) combine gradually in diffused daylight, but explode violently if exposed to direct sunlight or heated,

$$H_2 + Cl_2 = 2HCl.$$

Hydrogen and *iodine* (p. 308) combine only partially, even at a red heat,

$$H_2 + I_2 \rightleftharpoons 2HI.$$

(*c*) *Combination with other Non-metals.*

(i) Hydrogen unites with molten sulphur to form sulphuretted hydrogen (p. 322),

$$S + H_2 \rightleftharpoons SH_2.$$

(ii) It combines reversibly with nitrogen to form ammonia,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3,$$

the combination being assisted by pressure and by the presence of catalysts (p. 379).

(iii) With carbon at a red heat it forms a small proportion of marsh gas (p. 447), whilst at the temperature of the electric arc acetylene is formed (p. 450).

$$C + 2H_2 \rightleftharpoons CH_4 \text{ (marsh gas)}$$
$$2C + H_2 \rightleftharpoons C_2H_2 \text{ (acetylene).}$$

(*d*) *Combination with Metals.*—Hydrogen unites directly with sodium, potassium, and calcium to form the HYDRIDES, NaH, KH, CaH_2 (pp. 558 and 625). It is also believed to unite with metals such as palladium, nickel, and copper, which act as catalysts in promoting the combination of hydrogen with organic compounds, *e.g.*, in presence of nickel

$$\underset{\text{Ethylene}}{C_2H_4} + H_2 = \underset{\text{Ethane}}{C_2H_6};$$

but as its solubility in these metals is very variable, any hydrides that may be formed are probably present in solid solution in the metal and not as a separate phase or layer. Arsenic and antimony combine with

hydrogen when the gas is generated in contact with these elements or their compounds,

$$As + 3H = AsH_3$$
$$Sb + 3H = SbH_3.$$

Hydrides of certain other metals, *e.g.*, copper, can be prepared by indirect methods.

Hydrogen as a Reducing Agent.

Hydrogen will remove oxygen from many metallic oxides, *e.g.*,

(i) $$CuO + H_2 = Cu + H_2O.$$

This reduction was used by Dumas in determining the composition of water, and is employed in the combustion of organic compounds.

(ii) $$Fe_3O_4 + 4H_2 \rightleftharpoons 3Fe + 4H_2O.$$

This action is the converse of the decomposition of steam by iron as described above.

(iii) The oxides of magnesium and sodium are not reduced by hydrogen, but on the contrary these metals are able to liberate hydrogen from steam.

The metals and their oxides can thus be divided into three groups as follows :—

Reduction of oxide by hydrogen, $CuO + H_2 \longrightarrow Cu + H_2O.$

Reduction of oxide and oxidation of metal, $Fe_3O_4 + 4H_2 \rightleftharpoons 3Fe + 4H_2O.$

Oxidation of metal by steam, $MgO + H_2 \longleftarrow Mg + H_2O.$

In the first group the action proceeds from left to right only and in the third group from right to left only; in the case of iron the action is reversible.

Many agents which liberate hydrogen are able to effect reductions which cannot be brought about by hydrogen itself. These reductions were formerly attributed to the special activity of hydrogen at the moment of its birth, but this explanation cannot be maintained in view of the fact that " nascent hydrogen " from different sources may behave in different ways and may even give rise to different products of reduction. Thus, tin and hydrochloric acid reduce nitric acid to hydroxylamine, NH_3O, whilst zinc and caustic soda give ammonia instead. Examples of reduction brought about by agents liberating hydrogen, but not by hydrogen gas under ordinary conditions, are :

(i) *Preparation of Arseniuretted Hydrogen.*

$$As + 3H = AsH_3.$$

(ii) *Reduction of Ferric Chloride to Ferrous Chloride.*

$$FeCl_3 + H = FeCl_2 + HCl.$$

The activity of hydrogen gas can, however, be increased considerably by breaking it up into minute bubbles by passing it through a mem-

brane ; in this form it will effect many reductions which are not usually brought about by hydrogen gas.

Detection and Estimation of Hydrogen.

Gaseous hydrogen when mixed with other gases can be detected and estimated by cooling the gas with liquid air in contact with charcoal, when all other gases except helium and neon are condensed completely. It can be identified most readily by means of its spectrum, which contains a series of four strong lines; these correspond with the "Fraunhofer lines" A, C, F, and G, and appear as black lines in the solar spectrum. In combination it can be detected by oxidation to water ; this method also serves for its estimation (p. 102).

Equivalent and Atomic Weight.

The equivalent and the atomic weight of hydrogen were formerly taken as unity. When the standard was altered so that the equivalent of oxygen became 8 and its atomic weight 16 exactly, the equivalent and the atomic weight of hydrogen were deduced from the composition of water (p. 90), the most probable value for these constants being 1·0075.

CHAPTER XXI

8. OXYGEN. O = 16

Occurrence of Oxygen.

Oxygen is by far the most abundant of the elements. In the free state it forms 23 per cent. by weight, or 20·9 per cent. by volume, of the atmosphere, whilst in combination it forms 88·8 per cent. of water or 86 per cent. of the ocean, and nearly 50 per cent. of the earth's crust (to a depth of ten miles), including the ocean and the atmosphere.

Preparation of Oxygen.

(*a*) *Separation from Liquid Air.*—At the present time oxygen is prepared commercially by the fractional distillation of liquid air (p. 373). The product contains 99 per cent. or more of oxygen, and is compressed into steel cylinders for transport.

(*b*) *Decomposition of Metallic Oxides.*

(i) The oxides of the noble metals are readily decomposed by heat. Thus very pure oxygen can be obtained by heating silver oxide, prepared by precipitation from a silver salt,

$$2Ag_2O = 4Ag + O_2.$$

A little caustic soda must be added to hold back any carbon dioxide that may be formed by the decomposition of silver carbonate (Ag_2CO_3) present as an impurity in the oxide.

(ii) The red oxide of mercury can be prepared by heating the metal in air at a temperature a little below its boiling-point, but it decomposes at a higher temperature. This decomposition led Priestley to his discovery of oxygen, whilst the reversible action indicated by a pair of arrows in the equation

$$2HgO \rightleftharpoons 2Hg + O_2$$

was used by Lavoisier (p. 63) to prove that combustion really consisted in the absorption of oxygen from the atmosphere by the burning substance.

(*c*) *Decomposition of Peroxides.*

(i) Scheele prepared oxygen by heating the black oxide of manganese,

$$3MnO_2 = Mn_3O_4 + O_2.$$

The product is an oxide, Mn_3O_4, analogous to, but not isomorphous with, the magnetic oxide of iron, Fe_3O_4.

(ii) Lead peroxide, PbO_2, when heated, decomposes into litharge, PbO, and oxygen,

$$2PbO_2 = 2PbO + O_2.$$

Red lead, which is intermediate between litharge and lead peroxide and may perhaps contain the oxide Pb_3O_4 (p. 693), also decomposes when heated strongly. It is prepared by heating litharge in air at 450° and yields litharge and oxygen at 550°.

(iii) The decomposition of barium peroxide by heat is a balanced action as shown in the equation

$$\underset{\text{Barium peroxide}}{2BaO_2} \rightleftharpoons \underset{\text{Baryta}}{2BaO} + O_2.$$

When heated above 800° under atmospheric pressure, barium peroxide is decomposed into baryta and oxygen, as shown by the upper arrow in the equation, since at this temperature the DISSOCIATION-PRESSURE of the oxygen set free by the dissociation of the peroxide rises above one atmosphere. On the other hand, when baryta is heated at a temperature of 500° in air at atmospheric pressure, barium peroxide is formed, the dissociation-pressure of the oxygen at this temperature being less than one-fifth of an atmosphere.

In BRIN'S PROCESS for the preparation of oxygen, which was in general use until 1908, the temperature of the baryta was kept constant at 700° and the absorption and expulsion of oxygen were brought about by variation of pressure. Purified air was pumped in under a pressure of about 10 lb. per square inch, the oxygen being absorbed by the baryta, whilst the nitrogen escaped by a safety valve. By reversing the pumps a vacuum of 26 inches of mercury (*i.e.*, a residual pressure of 4 inches of mercury) was produced; the barium peroxide then decomposed, and the oxygen (after rejecting the first portions) was transferred to a gas-holder. The two processes occupied about seven minutes each, or four cycles per hour. The oxygen obtained in this way contained about 96 per cent. of oxygen and 4 per cent. of nitrogen.

(iv) Peroxides also lose oxygen when converted into salts by the action of sulphuric acid, *e.g.*,

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + O_2 + 2H_2O,$$

whilst with hydrochloric acid they liberate chlorine. Sodium peroxide, which is decomposed by water,

$$2Na_2O_2 + 2H_2O = 4NaOH + O_2,$$

can be used as a source of oxygen. When used for renewing the air in confined spaces it has the merit of removing the carbon dioxide produced by breathing in addition to replacing the oxygen.

(v) In certain cases the lower oxides of a metal are basic and the higher oxides are acidic. These higher oxides, like the peroxides described above, liberate oxygen, and yield a salt of the lower basic

oxide when acted on by sulphuric acid, *e.g.*, in the case of potassium dichromate, $K_2Cr_2O_7$, chromic anhydride, CrO_3, is first set free, and then liberates oxygen and yields chromic sulphate, $Cr_2(SO_4)_3$.

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + H_2O + 2CrO_3,$$
$$2CrO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O + 3O, \text{ or}$$
$$K_2Cr_2O_7 + 4H_2SO_4 = 2KCr(SO_4)_2 + 4H_2O + 3O.$$

The oxygen liberated in this action can be used as a powerful oxidising agent (compare " nascent hydrogen," p. 226), or may escape as oxygen gas, O_2.

(*d*) *Decomposition of Salts.*—Many salts lose a part or the whole of their oxygen when heated. Thus :

(i) Potassium nitrate " boils " when heated, liberating one-third of its oxygen and giving a residue of potassium nitrite.

$$\underset{\text{Potassium nitrate}}{2KNO_3} = \underset{\text{Potassium nitrite}}{2KNO_2} + O_2.$$

(*ii*) Potassium chlorate melts at 360° and parts with the whole of its oxygen when heated to about 400°.

$$\underset{\text{Potassium chlorate}}{2KClO_3} = \underset{\text{Potassium chloride}}{2KCl} + 3O_2$$

In presence of small quantities of manganese dioxide, platinum black, or china clay the decomposition takes place below 240°. Substances such as these, which accelerate a chemical change but are themselves unchanged at the end of the action, are described as CATALYSTS. The oxygen prepared from potassium chlorate with the aid of catalysts contains traces of chlorine which may be removed by passing the gas through an aqueous solution of sodium hydroxide.

(iii) Potassium permanganate when heated gently gives potassium manganate, manganese dioxide, and oxygen.

$$\underset{\text{Potassium permanganate}}{2KMnO_4} = \underset{\text{Potassium manganate}}{K_2MnO_4} + MnO_2 + O_2.$$

(iv) Bleaching powder, which is prepared by combining dry slaked lime with chlorine (p. 633), is easily decomposed in such a way as to liberate the chlorine again ; but when a solution of bleaching powder is warmed with a cobalt salt to a temperature of 70° to 80°, oxygen is liberated instead.

$$\underset{\text{Bleaching powder}}{2CaOCl_2} = \underset{\text{Calcium chloride}}{2CaCl_2} + O_2.$$

The cobalt salt is described as a " catalyst," but in this case it alters the course of the reaction and not merely its velocity.

(v) Many salts, such as potassium dichromate, which do not decom-

pose readily when heated alone, liberate oxygen when acted on by strong sulphuric acid (see above).

(e) *By Electrolysis.*

$$2H_2O = 2H_2 + O_2.$$

Pure oxygen is prepared commercially, together with hydrogen (p. 223), by the electrolysis of an aqueous solution of caustic soda. Very pure oxygen and hydrogen can be prepared by the electrolysis of aqueous baryta (p. 245).

Physical Properties of Oxygen.

(a) *Gas.*—Oxygen is a colourless, odourless gas, which appears slightly bluish in thick layers when under pressure. Its density is 1·429 grams per litre at 0° and 760 mm. pressure. It is sparingly soluble in water, which dissolves 4 per cent. by volume of oxygen at 8°, as compared with 2 per cent. of nitrogen ; on account of the greater solubility of oxygen, air dissolved in water contains 34 per cent. of oxygen by volume instead of the 21 per cent. present in the atmosphere.

(b) *Liquid and Solid.*—Oxygen can be condensed to a pale steel-blue, mobile liquid boiling at − 183°. The "critical temperature," above which the gas cannot be liquefied even under very great pressures, is − 118° ; at this temperature a pressure of 50 atmospheres will liquefy the gas. When the liquid is evaporated very rapidly it solidifies to crystals which melt at − 227°.

Chemical Properties of Oxygen.

Oxygen forms compounds with all the elements except fluorine, bromine, and the rare gases of the atmosphere. For this reason, amongst others, oxygen is now preferred to hydrogen as a standard in determining the equivalents and atomic weights of other elements. Except in the case of the halogens and the noble metals, such as silver, gold, and platinum, oxides can be prepared by direct combination of the element with oxygen (p. 234).

Oxidation at Atmospheric Temperatures.

Whereas hydrogen will combine in the cold with only a few elements such as fluorine, chlorine (in the presence of light), and oxygen (in the presence of finely-divided palladium or platinum), gaseous oxygen is a very active gas which will combine in the cold with many elements and with a considerable number of compounds, whilst at a higher temperature many other substances will take fire and burn in the gas. The following are examples of oxidations which are brought about by atmospheric oxygen at normal temperatures.

(*a*) *Phosphorus* will smoulder and *iron* will rust in moist air (Scheele, 1774), absorbing the oxygen quantitatively :

$$\underset{}{P_4} + 3O_2 = \underset{\text{Phosphorous oxide}}{P_4O_6}$$

$$4Fe + 3O_2 = \underset{\text{Ferric oxide}}{2Fe_2O_3}.*$$

(*b*) *Nitric oxide*, NO, combines with oxygen to form brown, soluble fumes of nitrogen peroxide, NO_2 :

$$2NO + O_2 = 2NO_2.$$

(*c*) *Sulphurous acid*, H_2SO_3, is oxidised to sulphuric acid :

$$\underset{\text{Sulphurous acid}}{2H_2SO_3} + O_2 = \underset{\text{Sulphuric acid}}{2H_2SO_4},$$

and the sulphites derived from it are oxidised in a similar way to sulphates, *e.g.*,

$$\underset{\text{Calcium sulphite}}{2CaSO_3} + O_2 = \underset{\text{Calcium sulphate}}{2CaSO_4}.$$

Hydrosulphites (p. 580) are oxidised still more readily, and can be used in estimating oxygen dissolved in water.

(*d*) In the presence of sunlight aqueous *hydrochloric acid* is oxidised with the formation of chlorine water :

$$4HCl + O_2 \rightleftharpoons 2Cl_2 + 2H_2O.$$

This is a balanced action, since chlorine water loses its strength and becomes converted into hydrochloric acid and oxygen under precisely similar conditions.

(*e*) *Ferrous*, *stannous*, and *cuprous salts* are oxidised by air to ferric, stannic, and cupric salts :

$$\underset{\text{Ferrous sulphate}}{4FeSO_4} + 2H_2SO_4 + O_2 = \underset{\text{Ferric sulphate}}{2Fe_2(SO_4)_3} + 2H_2O.$$

$$\underset{\text{Stannous chloride}}{2SnCl_2} + 4HCl + O_2 = \underset{\text{Stannic chloride}}{2SnCl_4} + 2H_2O.$$

$$\underset{\text{Cuprous chloride}}{2Cu_2Cl_2} + 4HCl + O_2 = \underset{\text{Cupric chloride}}{4CuCl_2} + 2H_2O.$$

When no free acid is present basic salts or hydroxides are formed.

(*f*) In the presence of air, *copper* is slowly attacked by dilute sulphuric acid at atmospheric temperatures, as shown by the equation

$$2Cu + 2H_2SO_4 + O_2 = 2CuSO_4 + 2H_2O.$$

This action, carried out at 100°, is used for the commercial preparation of copper sulphate (p. 842).

(*g*) In presence of catalysts, such as finely-divided platinum or

* Iron rust also contains ferric hydroxide, $Fe(OH)_3$, and ferrous carbonate, $FeCO_3$.

palladium, oxygen will combine directly (without previous heating) with hydrogen and many compounds containing it (p. 225).

(*h*) *Organic compounds.*—(i) Turpentine and other "drying oils" are oxidised by air with formation of solid resins. (ii) The oxidation, following upon respiration, on which life depends also takes place at low temperatures. (iii) Pyrogallol in cold alkaline solution is used in gas analysis for the quantitative absorption of oxygen.

Combination of Oxygen with Non-metals.

(*a*) *Sulphur.*—Sulphur burns in air to sulphur dioxide,

$$S + O_2 = SO_2$$

When burnt in oxygen instead of air, sulphur also yields small quantities of sulphur trioxide,

$$2S + 3O_2 = 2SO_3.$$

The oxidation of sulphur dioxide to sulphur trioxide can be brought about by air acting in the presence of finely divided platinum (p. 333),

$$2SO_2 + O_2 = 2SO_3.$$

(*b*) *Phosphorus.*—Phosphorus smouldering in air gives rise to phosphorous oxide, P_4O_6, and phosphorous acid, H_3PO_3,

$$P_4 + 3O_2 = P_4O_6$$
$$P_4O_6 + 6H_2O = 4H_3PO_3.$$

When burnt in a liberal supply of air or oxygen, the higher oxide, phosphoric anhydride, P_4O_{10}, is formed :

$$P_4 + 5O_2 = P_4O_{10}.$$

(*c*) *Carbon.*—Carbon burns in air or oxygen to carbon dioxide :

$$C + O_2 = CO_2.$$

The lower oxide, carbonic oxide, CO, is not produced directly by burning carbon in a limited supply of oxygen, but is formed readily by the further action of carbon on the dioxide :

$$C + CO_2 = 2CO.$$

(*d*) *Silicon* and *Boron* will also burn in oxygen :

$$Si + O_2 = SiO_2$$
$$4B + 3O_2 = 2B_2O_3.$$

(*e*) *Chlorine, Bromine,* and *Iodine* do not combine directly with oxygen, although oxides of chlorine and iodine may be prepared by indirect methods.

(*f*) *Nitrogen.*—At the temperature of the electric arc nitrogen and oxygen combine to form nitric oxide,

$$N_2 + O_2 \rightleftharpoons 2NO.$$

When the temperature falls below 800°, a further oxidation to nitrogen peroxide takes place,

$$2NO + O_2 = 2NO_2.$$

Combination of Oxygen with Metals.

The behaviour towards oxygen of some of the principal metals is shown in the following table.

TABLE 29.—BEHAVIOUR OF THE METALS TOWARDS OXYGEN.

NOBLE METALS	Platinum, Gold, Silver	Do not oxidise in air; oxides decompose when heated.
	Mercury	Oxide formed by gentle roasting, decomposes when heated more strongly.
BASE METALS	Copper	Finely-divided metal burns in oxygen.
	Lead, Tin, Iron	Finely-divided metals burn in air.
	Zinc	Metal burns in air.
	Aluminium	Amalgam oxidises in air.
	Magnesium, Sodium, Potassium	Metals burn in air and in steam.

Silver, although a noble metal which does not burn in air, possesses the property of absorbing oxygen when molten and liberating it when the metal solidifies; this is probably due to the formation of an oxide, Ag_2O, which dissolves in the molten metal but is thrown out from it and at once decomposed when the metal crystallises (p. 847).

Mercury, the oxidation of which is a reversible action (p. 65),

$$2Hg + O_2 \rightleftharpoons 2HgO,$$

is intermediate between the noble and the base metals.

Copper, when heated in air or oxygen, is converted into cupric oxide, CuO; the porous copper obtained by reducing this oxide in a current of hydrogen takes fire and burns when heated in oxygen.

Lead readily oxidises when melted in a current of air, and forms litharge, PbO; finely-divided lead, prepared by heating the tartrate, is "pyrophoric," that is, it catches fire on exposure to air.

Iron oxidises to smithy scale, Fe_3O_4, when heated in air, but without incandescence. Fine iron wire can, however, be burnt in oxygen by using a small fragment of burning sulphur or wood to ignite it. Iron filings will burn in a flame, and the finely-divided iron made by heating the tartrate is "pyrophoric" like finely-divided lead. The ignition of "tinder" by means of a flint and steel depends on the burning of tiny particles of iron struck off from the steel by contact with the flint. An alloy of iron with rare metals such as cerium (p. 668), known as "pyrophoric alloy," is used instead of steel to ignite methyl alcohol or petrol in the "lighters" now often used as substitutes for matches.

Zinc foil can be set on fire by means of a blowpipe, but does not burn readily unless heat is applied continually, as when zinc is burnt to produce "zinc white," ZnO, for use as a pigment. *Aluminium* burns brilliantly like zinc if heated continuously, giving the oxide Al_2O_3. *Magnesium*, on the other hand, burns continuously to the white oxide, MgO, when ignited in air.

Sodium and *potassium* burn in air or oxygen to the peroxides, Na_2O_2 and K_2O_4.

When the metals are arranged in the order shown in the table, it will be noticed that the readiness with which oxidation takes place increases on passing down the series. The action shown by the equation

$$\text{Metal} + \text{oxygen} \rightleftarrows \text{metallic oxide}$$

proceeds in the sense of the upper arrow in the case of platinum and gold, and in the sense of the lower arrow from copper to potassium; it is reversible as indicated by the two arrows in the case of mercury and perhaps of silver.

A similar statement can be applied to the interaction of the metals with water. If this be represented by the equation

$$\text{Metal} + \text{steam} \rightleftarrows \text{metallic oxide} + \text{hydrogen},$$

the action proceeds in the sense of the upper arrow in the case of the metals from platinum to tin and in the sense of the lower arrow in the case of the metals from zinc to potassium. In the case of iron the action is a balanced one.

This arrangement of the metals can also be used to indicate the general action of the acids. Thus the metals from tin downwards are, as a rule, soluble in dilute acids, whilst the metals from lead upwards are insoluble. Concentrated sulphuric acid and dilute nitric acid, which are oxidising agents as well as acids, dissolve lead, copper, mercury, and silver; and, finally, "aqua regia" (p. 286), which is a chlorinating agent as well as an acid, will dissolve also the two metals, gold and platinum, which are placed at the top of the table.

Oxygen as an Acidifying Agent.

The name oxygen was introduced by Lavoisier to express the fact that the oxides of the non-metals possess acid properties. The fact that the oxides of the metals are basic was ignored, perhaps because at that time it was not known definitely that the strongest bases, such as lime and the alkalies, contained oxygen. The acid-producing power of oxygen is, however, shown by the tendency of the metals, as the proportion of oxygen in their oxides is increased, to give acidic rather than basic oxides. Thus, whilst chromic oxide, Cr_2O_3, and manganous oxide, MnO, possess basic properties, chromium trioxide, CrO_3, and dimanganese heptoxide, Mn_2O_7, are acid anhydrides from which important series of salts are derived. In the same way, the

higher oxides of the non-metals give stronger acids than the lower oxides ; thus, sulphuric acid, H_2SO_4, is stronger than sulphurous acid, H_2SO_3, and nitric acid, HNO_3, is stronger than nitrous acid, HNO_2.

Oxidation by Oxygen in the Presence of a Catalyst.

(*a*) *Metallic Catalysts.*—Oxygen, like hydrogen, becomes much more active in the presence of finely-divided metals. Not only will oxygen and hydrogen combine together at low temperatures in the presence of palladium and platinum, but finely-divided platinum is also used on a very large commercial scale to promote the combination of sulphur dioxide and oxygen (p. 333) as shown by the equation

$$2SO_2 + O_2 = 2SO_3.$$

This does not take place to any appreciable extent in the absence of a catalyst. Platinum gauze is also used industrially to promote the burning of ammonia to steam and nitric oxide (p. 383),

$$4NH_3 + 5O_2 = 4NO + 6H_2O.$$

(*b*) *Other Catalysts.*—Many other substances besides the metals possess the property of promoting oxidation. Thus, the combustion of coal gas takes place with greatly increased readiness in contact with a hot surface of earthenware or fireclay. This has been used on a large technical scale in heating boilers by means of producer gas (p. 467) mixed with air. Again hydrogen and oxygen, which combine only slowly at 500°, unite readily without flame or explosion in presence of a large porous surface of firebrick, complete combination of the oxygen and hydrogen taking place at 420°. *Ferric oxide* can also be used to promote the combination of sulphur dioxide with oxygen, although it is less effective than platinum, and *copper salts* are used to promote the oxidation of hydrogen chloride by air (p. 270).

Oxidising Agents.

Although it is not customary to speak of nascent oxygen, there are many mixtures which will bring about oxidations that cannot be effected by means of gaseous oxygen. Amongst the principal oxidising agents, many of which are more efficient than oxygen gas, are the following :—

(*a*) *Ozone*, O_3, and *Hydrogen Peroxide*, H_2O_2 (pp. 263 and 260).—These two compounds may be regarded as oxygen and water to which an additional atom of oxygen has been attached so loosely that it possesses oxidising properties in excess of those of molecular oxygen.

(*b*) *Nitric Acid* and *Sulphuric Acid.*—These acids dissolve copper, mercury, and silver in virtue of their oxidising properties. The oxidation of carbon by means of boiling sulphuric acid is shown by the equation,

$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O.$$

In some cases the efficiency of these two oxidising agents is increased greatly by the presence of a mercury salt. Selenic acid (p. 359) is a still more powerful oxidising agent and will dissolve metallic gold.

(*c*) *Oxides of Chromium* and *Manganese*.—The higher oxides of chromium and manganese, and the salts derived from them, are used very largely as oxidising agents. Thus a mixture of sulphuric acid and potassium dichromate is used as a "depolariser" to oxidise hydrogen to water in the dichromate battery (see Fig. 78, p. 196, and compare p. 743), chrome alum, $KCr(SO_4)_2,12H_2O$, being formed as a waste-product:

$$6H + K_2Cr_2O_7 + 4H_2SO_4 = 2KCr(SO_4)_2 + 7H_2O.$$

(*d*) *Manganese dioxide* and *Lead peroxide* can both be used in the presence of an acid to bring about the oxidation of oxalic acid, $H_2C_2O_4$, to water and carbon dioxide,

$$PbO_2 + H_2C_2O_4 + 2HNO_3 = Pb(NO_3)_2 + 2H_2O + 2CO_2$$
$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2H_2O + 2CO_2.$$

(*e*) *Chlorine Water*.—Chlorine in the presence of water acts as a powerful oxidising agent; it is mainly to this fact that it owes its bleaching properties. The oxidation of sulphur dioxide by chlorine water is shown by the equation

$$Cl_2 + H_2O + SO_2Aq = 2HCl + SO_3Aq.$$

In this action the water molecule is torn apart by the affinity of chlorine for hydrogen and of sulphur dioxide for oxygen. Another example of this combined attack is found in the case of aluminium oxide, which is not decomposed by the action of carbon or of chlorine alone, but succumbs to the united action of these two agents as shown by the equation

$$3Cl_2 + Al_2O_3 + 3C = 2AlCl_3 + 3CO.$$

(*f*) *Electrolytic Oxidation*.—Many oxidations can be effected in contact with the anode of an electrolytic cell, where oxygen is liberated by the decomposition of water, *e.g.*,

$$NaClO_3 + O = NaClO_4.$$

Technical Applications of Oxygen.

Oxygen, compressed into steel cylinders for transport, is used in medicine to enrich the air when respiration is difficult. It is also used in the oxy-hydrogen blowpipe for working platinum and silica and for the production of LIMELIGHT (see below, p. 239). The oxy-acetylene blowpipe is used even more extensively for welding metals and for cutting through steel plates.

Detection and Estimation of Oxygen.

Free oxygen is recognised by its power of supporting combustion; it can be distinguished from nitrous oxide, N_2O, which is also a good

supporter of combustion, by the brown fumes which are produced when oxygen is mixed with nitric oxide,

$$2NO + O_2 = 2NO_2.$$

Free oxygen can be estimated

(i) By sparking with an excess of hydrogen.

(ii) By mixing with hydrogen and passing over spongy palladium, when one-third of the diminution of volume represents oxygen.

(iii) Volumetrically by absorption, *e.g.*, in an alkaline solution of pyrogallol or by an ammoniacal solution of cuprous chloride, Cu_2Cl_2.

(iv) Gravimetrically by absorption by metallic copper.

Oxygen dissolved in water can be titrated by means of a solution of sodium hydrosulphite, $Na_2S_2O_4$; as this reducing agent decolorises indigo, a solution of indigosulphonic acid (prepared by dissolving indigo in fuming sulphuric acid and then diluting with water) is used as an indicator; when the action is complete the indigo is bleached by the excess of hydrosulphite.

Oxygen in combination may be detected as water or carbon dioxide by reducing the oxide with hydrogen or carbon or with compounds of these elements; the quantity of combined oxygen is usually determined "by difference" after estimating the other elements that are present.

As oxygen is now taken as the standard of equivalents and atomic weights, the experiments formerly used to determine the equivalent and atomic weight of oxygen are now used to deduce these constants for hydrogen.

COMBUSTION.

Combustion in Oxygen, Chlorine, Sulphur, Hydrogen, etc.

Whenever sufficient heat is liberated by a chemical change to produce visible light, the substances undergoing change are said to "burn," *e.g.*, carbon "burns" in oxygen with a brilliant incandescence. Burning, however, does not necessarily imply combination with oxygen; thus—

(i) Phosphorus ignites spontaneously and burns in *chlorine*, forming phosphorus trichloride, PCl_3. So, also, finely-divided arsenic, antimony, copper, tin, lead, and iron burn in chlorine, forming chlorides of these elements. When silica burns in fluorine, oxygen is actually displaced by the halogen from combination with silicon and liberated in the elementary state.

(ii) When copper and iron are heated with *sulphur*, the sulphides of these metals are formed with brilliant combustion.

(iii) Red lead will take fire and burn with incandesence when heated in *hydrogen*. Metallic lithium will also burn with incandescence in hydro-

gen, forming the hydride, LiH, and metallic cerium and uranium will burn with brilliant incandescence in *nitrogen*.

(iv) Finally, magnesia will burn with brilliant incandescence when heated in the vapour of *sulphur trioxide* (Fig. 105), magnesium sulphate being formed as shown in the equation

$$MgO + SO_3 = MgSO_4.$$

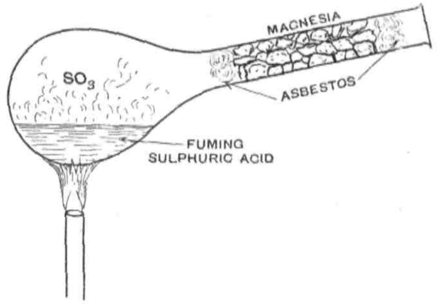


FIG. 105. COMBUSTION OF MAGNESIA IN SULPHUR TRIOXIDE.

Flame.

(*a*) *Flames produced by Burning Gases.*—When two gases burn together the hot gas which is produced by their combustion is described as a FLAME. Thus, a flame may be produced either by burning coal-gas in air or by burning air in coal-gas, as may be shown by using the apparatus represented in Fig. 106. Again, whilst carbon, which cannot be vaporised except at very high temperatures, burns in oxygen without a flame, sulphur and phosphorus, which are easily vaporised, burn, the one with a pale blue flame and the other with a brilliant, luminous flame.

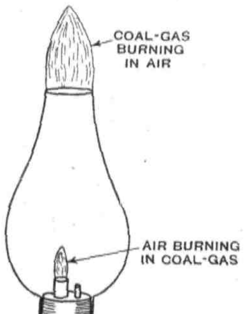


FIG. 106.—BURNING OF COAL-GAS AND AIR.

The gas is lighted at the tip of the L-shaped glass tube and the lamp glass is then placed in position. The gas is then turned on full, when the gas-flame moves to the top of the lamp-glass, whilst an air-flame appears at the top of the air-tube.

(*b*) *Temperature of Flames.*—The maximum temperatures of various flames, as measured by a small thermo-couple placed in the hottest part of the flame, are said to be as follows :

Bunsen burner, 1870°.
Air blowpipe, 2200°.
Oxy-hydrogen blowpipe, 2400°.
Oxy-acetylene blowpipe, 2600°.

For comparison, the following estimated temperatures may be quoted :

Electric arc, 3300°. Sun, 8000°.

(*c*) *Luminosity due to Hot Solids.*—The intensely hot oxy-hydrogen flame is almost invisible when burning under atmospheric pressure owing to the poor radiating power of the gases, but a brilliant incandescence is produced when the flame is directed against a block of lime, as in the LIMELIGHT LANTERN. So, also, the almost invisible flame produced by burning a mixture of coal-gas and air is made to

produce a brilliant light by inserting in the flame an INCANDESCENT MANTLE (composed mainly of thorium dioxide, ThO_2, mixed with about 1·5 per cent. of cerium sesquioxide, Ce_2O_3, p. 680), which emits a very high proportion of visible light rays at the temperature of the flame.

Many luminous flames owe their luminosity to solid particles formed during combustion. Thus, the flame of the BATSWING-BURNER, in which coal-gas was burned directly in air, owed its luminosity, at least *in part, to the presence of solid particles of unburnt carbon, or soot, in* the smoky flame. Special coal was selected for the manufacture of the gas, in order to ensure the presence in the gas of hydrocarbons to produce the necessary soot; burners were also constructed in which the gas was enriched by naphthalene (p. 446) vaporised by the heat of the flame.

The flame of nickel carbonyl, $Ni(CO)_4$, from which metallic nickel is deposited readily on a cold piece of porcelain, is highly luminous. On the other hand, the flame of antimoniuretted hydrogen, SbH_3, is practically non-luminous, although it deposits metallic antimony upon a cold surface.

(*d*) *Luminosity of Hot Gases.*—In some cases a luminous flame is produced when solid particles would not be expected to appear in the flame; thus, phosphoretted hydrogen, PH_3, carbon disulphide, CS_2, and arsenic burn in oxygen with luminous flames, although the products of combustion are all gaseous at the temperature of combustion. Again, some non-luminous mixtures burn brilliantly when the constituents are heated before combustion; *e.g.*, marsh gas and air, if passed through red-hot tubes, burn together with a very luminous flame.

Luminosity can also be produced by compression. Thus, the flames of alcohol-vapour and of hydrogen burning in air become luminous under pressure. Conversely, a candle burns in a partial vacuum with a very feebly luminous flame.

Structure of Flame.

When coal-gas is to be used as a source of heat, or to produce light indirectly with the help of an incandescent mantle, special methods are used to burn the soot completely, and thus to give a clean and almost invisible flame. This is done by mixing the gas with a considerable quantity of air as in the burners shown in Figs. 107 to 110.

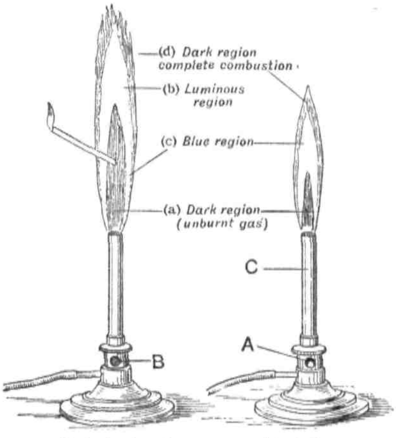
(*a*) In the Bunsen Burner (Fig. 107) coal-gas is admitted through a narrow pin-hole in a nipple at *A*. The stream of gas flows past an adjustable opening at *B* and draws in a quantity of air which can be varied by regulating the opening. The mixture of gas and air passes up the tube *C* and is ignited at the top. The air introduced at *B* may be called the "primary air," whilst the atmosphere supplies "secondary air" to the flame.

(i) When the primary air is cut off, by closing the opening at *B*, the gas burns with a luminous flame at the top of the tube *C*. This flame includes

a thin outer non-luminous cone *d* of a blue colour, in which combustion takes place with the help of the secondary air, whilst the interior of the cone is occupied in part by a luminous region *b* in which the hydrocarbons in the gas are decomposed and raised to a high temperature by the hot shell of flame outside. The fact that the cone in which combustion takes place is hollow can be proved by inserting a narrow tube, and igniting at the upper end of this tube the unburnt gas drawn off from the interior of the flame.

(ii) When primary air is introduced into the gas, the outer zone of complete combustion increases in thickness, the luminous region gradually disappears, and an inner cone, *c*, of a lighter colour is seen. In this inner cone the gas is partially burnt with the help of the primary air, the combustion being completed with secondary air in the outer region of the flame.

(iii) When a lower cone is formed, the mixture of gas with primary air is within the "limits of inflammability," that is, the mixture can sustain a flame without the aid of secondary air. Such a mixture, if ignited at one point in a very long tube, will burn slowly and quietly for a distance of about 50 centimetres, but vibratory movements then commence and finally set up an explosive wave which travels along the tube at a velocity of from 1500 to 3500 metres per second. In the inner cone of the flame of a Bunsen burner the flame is continually travelling downwards in the mixture of gas and air, but the velocity of propagation downwards is less than the upward velocity of the mixture. If, however, the quantity of primary air be increased still further, the velocity of propagation will increase until it exceeds the rate of flow of the gas in the tube; when this occurs the inner cone will travel down the tube and burn at the bottom. The flame in this position is described as having "struck back."



Air-hole closed. Air-hole open.
FIG. 107.—BUNSEN BURNER (common form).

(*b*) The more completely the gas is burnt by the primary air, the hotter is the flame; but when the supply of primary air is almost sufficient to produce complete combustion there is a great tendency for the flame to strike back. This may be checked by maintaining a high velocity in the inflammable mixture; uniform mixing and uniform velocity of flow are also of great service in helping to increase the quantity of air that can be admitted before the flame strikes back. Thus,

(i) A very hot flame can be produced by means of the Teclu burner (Fig. 108), in which the gas passing up the tube *C* sucks in air through the gap *B*, which extends right round the burner, so that the primary air is mixed uniformly with the gas. The proportion of air is controlled by a plate mounted on a screw, *D*, by means of which the width of the inlet gap can be altered.

(ii) Striking back may also be prevented by covering the top of the burner

with wire gauze as in Fig. 109; this conducts away the heat of the flame so that the gases below the gauze never reach the "*ignition point*"; the air inlet may also be covered with gauze to prevent ignition at this point. Davy's safety lamp for miners is an application of the same principle. The flame is here surrounded completely by a cylinder made of fine wire gauze. The "firedamp" which passes through the gauze burns with a characteristic flame known as the "corpse light"; but, owing to the high heat-conductivity of the gauze, the flame cannot pass through it to the inflammable mixture outside.

(iii) A nickel grid, about a centimetre thick, is a more efficient means for *preventing "striking back."* This is used in the Méker burner shown in Fig. 110. The air inlet consists of several holes extending all round the burner, and the top of the burner is expanded so as to ensure uniform mixing of the gas and primary air. With large air-inlet holes, the quantity of primary air is sufficient to burn the gas completely, so that the flame above the grid consists

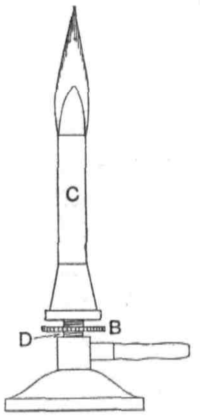


FIG. 108.—TECLU BURNER.

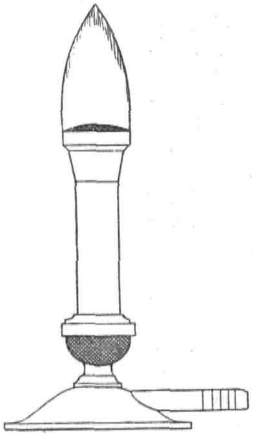


FIG. 109.—BUNSEN BURNER WITH GAUZE.

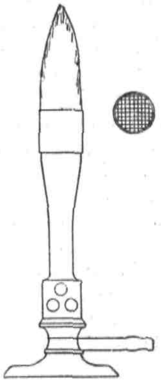


FIG. 110.—MÉKER BURNER.

of a very compact single "solid" cone, which corresponds with the outer cone of the ordinary Bunsen flame. If the primary air be decreased gradually, by covering the air-holes one by one, minute cones appear over each section of the grid and finally coalesce into a single inner cone; when the air supply is still further reduced, the inner cone first becomes indefinite, and then a luminous flame is obtained. The ordinary blowpipe flame is a solid one, similar to the Méker flame, with the base blown into the form of a cone.

Fig. 111 shows a series of photographs obtained by increasing gradually the supply of air and then of gas to a Bunsen burner. In I, where the supply of gas is very small, the flame consists of a hollow, bright blue inner cone, *a*, surrounded by a lilac-coloured border, *c*. When more gas is used, a luminous spot, *b*, appears as in II, and increases in size until it occupies the greater part of the flame as in IV. When the supply of air is now increased, the luminous or yellow region, *b*, decreases again, as in V and VI, and finally disappears, as in VII, which shows the usual dark inner cone, *a*, and faintly luminous outer cone, *d*, of the Bunsen flame, separated by a thin blue cone,

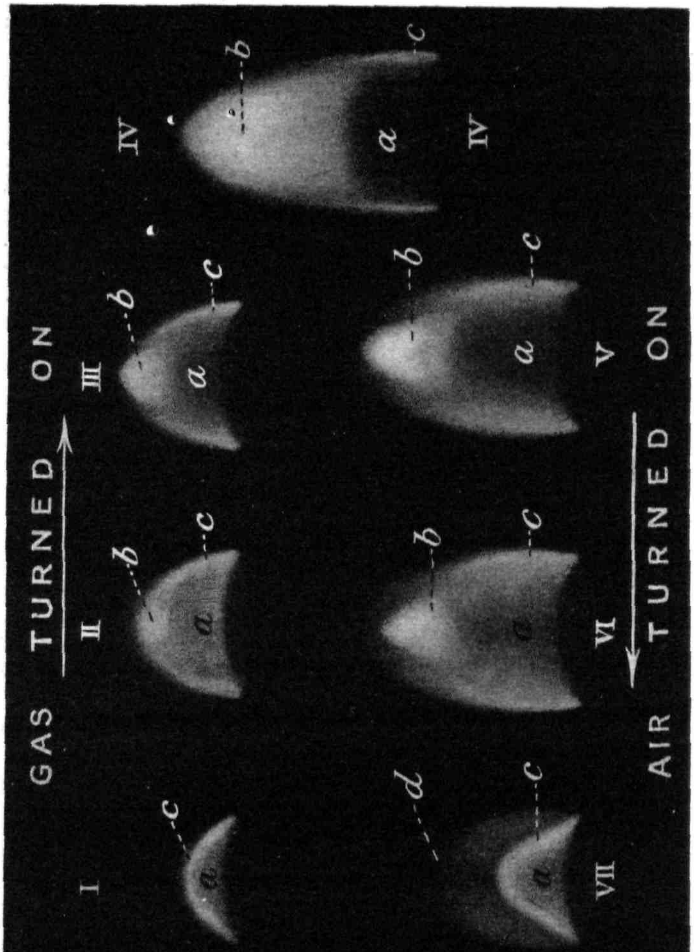


FIG. 111.—ANALYSIS OF FLAME OF BUNSEN BURNER. (Smithells).
a = dark region. b = yellow region. c = blue region. d = faintly luminous region.

c. The flames shown in I and VII are very similar to one another, but differ in the presence of a large faintly luminous region, *d*, in the normal flame VII.

Temperature of Ignition.

An essential feature of combustion is the liberation of heat. This increases rapidly as the rate of combustion increases with the temperature of the gas. At low temperatures the heat liberated by combus-

tion is usually not sufficient to compensate for the heat lost by conduction and radiation ; the combustible material therefore cools and combustion ceases. When the temperature is raised, the rate of combustion increases, until a temperature is reached at which the liberation of heat by combustion exceeds the loss due to conduction and radiation ; the substance will then continue to burn even when no external heat is supplied. This temperature is called the IGNITION-POINT.

A few substances such as the liquid hydride of phosphorus, P_2H_4, and zinc ethyl, $Zn(C_2H_5)_2$, take fire spontaneously in air at atmospheric temperatures. Phosphorus commences to glow at 7° and ignites at 60°. The vapour of carbon disulphide ignites at 120°, but glows before the ignition point is reached. The ignition points for some of the commoner gases when mixed with enough oxygen for complete combustion have been determined as follows :—

TABLE 30.—IGNITION TEMPERATURES OF GASES.

Hydrogen	585°
Carbon monoxide (moist)	650°
Methane	700°
Ethylene	510°
Acetylene	430°

Limits of Inflammability.

In the case of mixtures of combustible gases with air or oxygen, the proportions within which a self-sustained flame may be excited are called the LIMITS OF INFLAMMABILITY. These limits depend to a considerable extent on the conditions, *e.g.*, wider limits are found in a vertical than in a horizontal tube and in a wide than in a narrow tube. The limits of inflammability for certain common mixtures are as follows :—

TABLE 31.—LIMITS OF INFLAMMABILITY OF GASEOUS MIXTURES.

Air and hydrogen	Air > 26 per cent.	H_2 > 4 per cent.
Air and carbon monoxide	Air > 26 per cent.	CO > 12½ per cent.
Air and methane	Air > 85 per cent.	CH_4 > 5 per cent.
Air and coal-gas	Air > 79 per cent.	Gas > 7 per cent.

Combustion in Dry Gases.

Dixon, in 1880, found that dry carbon monoxide would not burn in dry oxygen ; a spark could be passed through the dry mixture without causing explosion, and on plunging a jet of burning carbon monoxide into dry oxygen the flame was extinguished. A few years afterwards Cowper observed that Dutch metal did not tarnish in carefully dried chlorine, although the alloy burns brightly in moist chlorine. Baker was able to heat carbon to redness, and to distil sulphur and phosphorus, in dry oxygen, without oxidation taking place. Armstrong, in 1885, put forward the theory that all chemical changes

are electrolytic in character, and take place by the co-operation of three distinct substances, at least one of which must be an electrolyte. He predicted that "Some day it would be ascertained that a mixture of pure oxygen with pure hydrogen was not explosive." He also pointed out that as absolutely pure water is not an electrolyte, it should not influence the combustion of pure hydrogen and pure oxygen; to be effective, the water must be sufficiently impure to render it conducting. These predictions were verified in a remarkable manner by Baker in 1902.

The apparatus used by Baker is shown in Fig. 112. A hard glass tube was filled with a dried mixture of pure hydrogen and oxygen, prepared by the electrolysis of a solution of barium hydroxide, and was closed by means of a plug of fusible metal. The tube, which contained a small quantity of phosphoric oxide, was either bent over at the top for heating with a burner or carried a coil of silver wire sealed into the glass. After leaving the gases to dry in the dark for ten days, the tube could be heated with a Bunsen burner, or the coil of silver wire melted (at 960°) by an electric current, without causing an explosion, although the partially dried mixture explodes when heated to 600°. A white-hot platinum wire, or large electric sparks, however, always brought about explosion. When the gases were heated after drying for two days only, visible drops of water were formed, but no explosion took place, probably because the water formed was so pure that it did not act as an electrolyte.

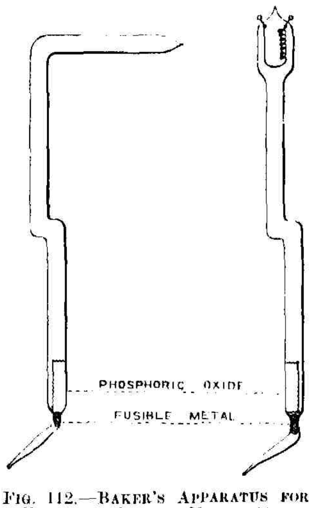


FIG. 112.—BAKER'S APPARATUS FOR HEATING DRIED MIXTURES OF HYDROGEN AND OXYGEN.

CHAPTER XXII

WATER, HYDROGEN PEROXIDE, AND OZONE

A. WATER.

Empirical formula, $H_2O = 18{\cdot}015$.

Occurrence.

(*a*) *Distribution of Water*.—Water in the free state forms about 96½ per cent. of the ocean and is also present in varying proportions in the atmosphere, and as underground waters in the solid crust of the earth. In the combined state it is found as "water of crystallisation" in minerals such as gypsum, $CaSO_4,2H_2O$, and in combination with silica in sedimentary deposits such as clay and shale, as well as in metamorphic rocks, such as serpentine, which liberate water when heated ; the elements of water are also present to the extent of nearly 2 per cent. (mainly in the form of mica) in deep-seated igneous rocks which have crystallised at high temperatures but under very high pressure. This water is lost when igneous rocks are erupted in a molten state as lava ; it is therefore not unlikely that hot springs may be fed by JUVENILE WATERS, distilled out for the first time from igneous rocks, or released from sedimentary and metamorphic rocks when carried down into regions of higher temperature.

(*b*) *Rain-water*.—The water-vapour of the atmosphere condenses out on cooling as RAIN, HAIL, or SNOW. RAIN-WATER is the purest of natural waters, containing as a rule only gaseous impurities, such as dissolved oxygen and nitrogen. The presence of carbon dioxide in rain-water is important, because it imparts to the water a solvent power which enables it to attack almost the whole range of igneous and sedimentary rocks. Rain-water also carries down combined nitrogen, mainly in the form of ammonium nitrate, to the extent of about 4 lb. of nitrogen per acre per annum, providing the original source for most of the fixed nitrogen of the soil and of vegetable and animal products. There is also an extensive circulation of salt spray from the sea, which is carried back again by rain.

(*c*) *Spring-water and River-water*.—Rain-water is always SOFT, *i.e.*, it readily forms a lather with soap ; but SPRING-WATER and RIVER-WATER contain additional impurities derived from the soil and rocks, which may make the water HARD, so that it gives a curd instead of

a lather with soap. These impurities include the bicarbonates, $Ca(CO_3H)_2$, $Mg(CO_3H)_2$, $Fe(CO_3H)_2$, of calcium, magnesium, and iron, which cause TEMPORARY HARDNESS, since they can be precipitated by boiling (p. 632), and the chlorides and sulphates of calcium and magnesium, $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, which give rise to PERMANENT HARDNESS. Spring-waters, which carry with them unusual impurities, such as sulphuretted hydrogen, exceptional proportions of iron, or unusual mineral impurities, are known as MINERAL WATERS, whilst those which contain large quantities of carbon dioxide are known as SPARKLING or AERATED WATERS; some of these exceptional impurities may be brought up from a considerable depth by waters penetrating from the surface, or may even be derived directly from deep-seated rocks by the action of "juvenile waters."

(*d*) *Sea-water.*—SEA-WATER contains about 3·6 per cent. of soluble salts (p. 559) washed out from the land and consisting mainly of common salt or sodium chloride, NaCl. There are, however, some marked points of contrast between the saline impurities of river-water and of sea-water; thus, in river-water the acid radicals are in the order

carbonates, sulphates, chlorides,

and the metallic radicals are in the order

calcium, magnesium, sodium,

but this order is reversed in sea-water. The contrast may be due to a large excess of salt in the primitive ocean, or to the precipitation of chalk from the ocean by living organisms to form sedimentary rocks such as chalk and limestone. Again, in igneous rocks the alkalies are approximately in the ratio $Na : K = 1 : 1$; in river-water the ratio is $Na : K = 1 : \frac{1}{4}$, a considerable proportion of the potassium being retained by the clay in the soil; in sea-water the proportion is $Na : K = 1 : \frac{1}{30}$ only, perhaps because the potassium is precipitated with ferric iron as glauconite, $KFeSi_2O_6$ (p. 762).

Formation of Water.

Water is produced by the combustion of hydrogen, and of compounds containing hydrogen, either in air or in oxygen or by means of oxidising agents such as copper oxide. Water is also formed as a by-product of the preparation of salts by the neutralisation of an acid with a base, *e.g.*,

$$\underset{\text{Litharge}}{PbO} + \underset{\text{Hydrogen chloride}}{2HCl} = \underset{\text{Lead chloride}}{PbCl_2} + \underset{\text{Water}}{H_2O}.$$

No water is produced however, when a salt is formed by the direct combination of two oxides, *e.g.*,

$$\underset{\text{Magnesia}}{MgO} + \underset{\text{Sulphur trioxide}}{SO_3} = \underset{\text{Magnesium sulphate}}{MgSO_4},$$

or by the combination of two hydrides, *e.g.*,

$$\underset{\text{Ammonia}}{NH_3} + \underset{\text{Hydrogen chloride}}{HCl} = \underset{\text{Ammonium chloride}}{NH_4Cl},$$

and water is actually absorbed when a salt is formed from a basic hydride and an acid oxide, *e.g.*,

$$\underset{\text{Ammonia}}{2NH_3} + H_2O + \underset{\text{Sulphur trioxide}}{SO_3} = \underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4}.$$

Physical Properties of Water.

(*a*) *Boiling-point and Freezing-point.*—The boiling-point and freezing-point of water under atmospheric pressure are used as the principal fixed points of the common scales of temperature, thus,

	Centigrade.	Fahrenheit.
Boiling-point .	100° C.	212° F.
Freezing-point .	0° C.	32° F.

The CRITICAL TEMPERATURE of water, above which it cannot be retained in a liquid state, is 374°; at this temperature water has a density of only 0·329 and exerts a maximum vapour pressure or CRITICAL PRESSURE of 217 atmospheres. The VAPOUR PRESSURE falls to 84 atmospheres at 300°, 15 atmospheres at 200°, 1 atmosphere or 760 mm. at 100°, and 4·58 mm. at 0°.

The freezing-point of water is lowered by pressure to the extent of 0·007° per atmosphere; when sealed up in a vacuum, therefore, ice, water, and steam are in equilibrium together at a temperature of + 0·007° and under a pressure of 4·58 mm. The conditions of equilibrium for the various forms of water are shown diagrammatically in Fig. 7, p. 7.

(*b*) *Density.*—Water contracts from 0° to 4° and then expands again. The density of water in grams per cubic centimetre is

0·9999	at 0°
1 exactly	at 4°
0·958	at 100° and falls to
0·329	at 374°

The contraction of water between 0° and 4° and its very small coefficient of expansion at temperatures above 4° (only 4·2 per cent. expansion over a range of 96°) are attributed to chemical changes producing a contraction (p. 250), superposed on the ordinary expansion due to rise of temperature.

The density of ice, 0·9168 gram per c.c. at 0°, is less than that of water in the ratio of 11 to 12 almost exactly; but under very high pressures, exceeding 2000 atmospheres, water freezes to an ice which is denser than the liquid. This DENSE ICE, when cooled to the temperature of liquid air, can be preserved even when the pressure is removed; it is then found to sink in liquid air whilst ordinary LIGHT

ICE floats. When, however, the temperature rises to −150° the dense ice swells up; crumbles, and breaks down into particles of ordinary light ice. The conditions of equilibrium for the various forms of ice are shown in Fig. 113.

(*c*) *Specific Heat.*—The heat-capacity of water is used as a standard for the measurement of quantity of heat; thus the heat required to raise the temperature of 1 gram of water from 15° to 16° is described as a small CALORIE. The specific heat of water varies, however, with the

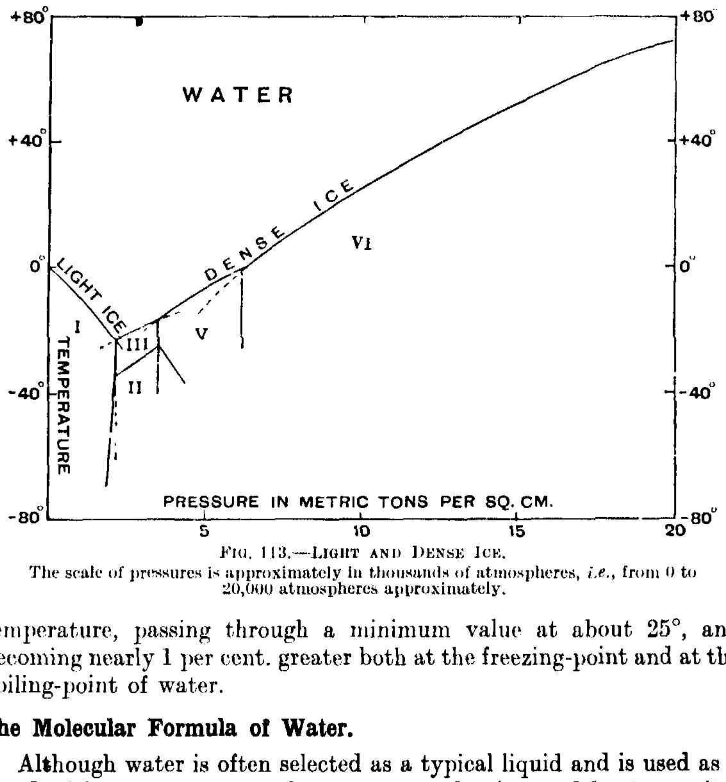


FIG. 113.—LIGHT AND DENSE ICE.
The scale of pressures is approximately in thousands of atmospheres, *i.e.*, from 0 to 20,000 atmospheres approximately.

temperature, passing through a minimum value at about 25°, and becoming nearly 1 per cent. greater both at the freezing-point and at the boiling-point of water.

The Molecular Formula of Water.

Although water is often selected as a typical liquid and is used as a standard in measurements of temperature, density, and heat-capacity, its properties are more anomalous than those of any other liquid. Thus, the boiling-point and freezing-point of water are exceptionally high for a compound of molecular weight 18, as may be seen by comparing water with some related compounds thus :

	Formula.	Mol. wt.	F.-pt.	B.-pt.
Water	OH_2	18	0°	100°
Ammonia	NH_3	17	− 78°	− 33°
Methane . . .	CH_4	16	−184°	−160°

Its contraction by heat in the range from 0° to 4° is also an unique property of water, and its specific heat and latent heat of evaporation and fusion are far higher than those of any other common liquid.

Most of these anomalies can be attributed to a REVERSIBLE POLYMERISATION (compare pp. 322 and 413), whereby the simple molecules of the formula H_2O which are present in steam become associated together into more complex molecules when cooled, but dissociate again into the simpler molecules when heated. Thus (i) the vapour density of *steam*, which at higher temperatures corresponds with the simple formula H_2O, increases slightly in the immediate neighbourhood of the boiling-point, probably because of the formation of molecules such as H_4O_2. (ii) *Liquid water* is certainly a mixture and may contain three or more kinds of molecules, *e.g.*, hydrol, H_2O, dihydrol, H_4O_2, trihydrol, H_6O_3. (iii) The two forms of *ice* are probably homogeneous compounds, *light ice* being perhaps H_6O_3, and *dense ice* H_4O_2. (iv) The high specific heat of water and its contraction between 0° and 4° may both be attributed to the dissociation of complex molecules (compare nitrogen peroxide, p. 413), as, for instance, the breaking down of "ice-molecules" (*e.g.*, H_6O_3) of low density into "water-molecules" (*e.g.*, H_4O_2) of higher density.

Water as a Solvent.

(*a*) Water is unique as a solvent, especially for the group of metallic salts. Its solvent properties are of supreme importance in the weathering of igneous rocks and their conversion into fertile soils, as well as in all the complex processes of vegetable and animal life. (*b*) Water is related in a special way to the *acids*, which contain hydrogen as a characteristic radical, to *alkalies* and *bases* which contain hydroxyl, $-OH$, or oxygen, and to the *salts* which are formed *along with water* when an acid and base are neutralised by one another (p. 247); for all these substances water is the only important solvent. Solutions of acids, bases, and salts in water are usually electrolytes (p. 190), that is, they carry an electric current and are decomposed thereby. This property is possessed also by molten salts and in exceptional cases by solutions in a few other IONISING SOLVENTS such as liquid sulphur dioxide, SO_2, liquid prussic acid, HCN, etc.

Properties of Aqueous Solutions.

(*a*) *Density.*—The process of dissolution is usually accompanied by contraction, especially in those cases in which chemical combination takes place between the solvent and the solute. In some aqueous solutions this contraction is very marked, *e.g.*, in the case of caustic soda, at all concentrations up to 12 per cent. NaOH the volume of the solution is actually less than that of the water which it contains; this is expressed by saying that the SOLUTION-VOLUME of the solute (*i.e.*, the volume of the solution containing 1 gram of the solute minus the original volume of the solvent used to dissolve it) is in this case actually

negative. In very rare instances, *e.g.*, ammonium chloride, NH_4Cl, and ammonium nitrate, $NH_4 \cdot NO_3$, the "solution volume" of the solute is greater than its "specific volume" in the solid state, and dissolution in water is accompanied by expansion.

(*b*) *Vapour pressure, Boiling-point, and Freezing-point.*—When the solute is not volatile, the vapour pressure of a solution is less than that of the solvent; its boiling-point is therefore higher, since a higher temperature is required to give a vapour pressure of one atmosphere. Conversely, the freezing-point is lowered by the presence of the solute. The LOWERING OF THE VAPOUR PRESSURE, the ELEVATION OF THE BOILING-POINT, and the DEPRESSION OF THE FREEZING-POINT are molecular properties, that is, equal numbers of molecules of different solutes produce equal effects. These properties can therefore be used (p. 169) in order to determine the molecular weight of substances which can be dissolved in water but cannot be vaporised.

(*c*) *Deliquescence.*—In the case of saturated solutions, the vapour pressure follows a well-defined curve, and over a narrow range of temperatures may be taken as a definite fraction of the vapour pressure of water. When the vapour pressure of a saturated solution is greater than the partial pressure of water-vapour in the air, the aqueous solution will evaporate; but when it is less, the solution will absorb water until the whole of the salt has dissolved, and the salt is said to be DELIQUESCENT. The humidity required to cause deliquescence in the case of some common salts is set out below as a percentage of the maximum vapour pressure of water at the same temperature.

TABLE 32.—HUMIDITY REQUIRED FOR DELIQUESCENCE OF SALTS.

	Temperature.	Solubility in grams per 100 grams of solution. Per cent.	Humidity required for deliquescence. Per cent.
Calcium chloride, $CaCl_2$	at 20°	43	43
Ammonium nitrate, $NH_4 \cdot NO_3$	at 20°	65	60
Sodium nitrate, $NaNO_3$	at 20°	47	73
Sodium chloride, $NaCl$	at 20°	27	76
Potassium nitrate, KNO_3	at 20°	24	95
Potassium chlorate, $KClO_3$	at 20°	6·8	99

Actual deliquescence depends quite as much on the moistness of the air as on the specific properties of the salt. In practice deliquescence of a salt is liable to occur if the relative humidity required for absorption of moisture is less than about 75 per cent., so that ammonium nitrate is freely deliquescent; sodium nitrate and sodium chloride are scarcely deliquescent when pure, and potassium nitrate is not usually classed as a deliquescent substance. Ammonium nitrate, which is deliquescent at 60 per cent. humidity, loses its water,

however, when stored in a warm room during the winter, owing to the drying of the air by condensation of moisture in the cold atmosphere outside; and even calcium chloride, which will absorb moisture from the air at a humidity of only 43 per cent., is no longer deliquescent in the very dry atmosphere of the laboratory during a cold winter in Canada.

Water of Crystallisation.

(*a*) *Formation of Hydrates.*—Many salts separate from aqueous solutions in combination with a definite molecular proportion of WATER OF CRYSTALLISATION. This can, as a rule, be removed from the salt without decomposing it, and restored to it by recrystallisation from water. Examples of salts crystallising with various proportions of water of crystallisation are:

Gypsum (calcium sulphate), $CaSO_4,2H_2O$.
Blue vitriol (copper sulphate), $CuSO_4,5H_2O$.
Schönite (potassium magnesium sulphate), $K_2Mg(SO_4)_2,6H_2O$.
Green vitriol (ferrous sulphate), $FeSO_4,7H_2O$.
Alum (potassium aluminium sulphate), $KAl(SO_4)_2,12H_2O$.

(*b*) *Vapour pressure and Efflorescence of Hydrates.*—Like water and ice, these hydrates have a definite vapour pressure which increases in a regular manner as the temperature rises. When the partial pressure of water-vapour in the air is less than its own vapour pressure, the hydrate will lose water and EFFLORESCE, that is, lose its crystalline form and break down into a powder. This powder may be either an anhydrous salt, or a hydrate containing a smaller proportion of water, which will decompose in its turn when the pressure of water-vapour in the air above it is reduced still further.

(*c*) *Stability of Hydrates.*—In some cases a series of hydrates is known each of which is stable in contact with the aqueous solution only over a limited range of concentrations. Two principal cases can then be distinguished:

(i) *The hydrate melts to a homogeneous liquid or solution when heated*, and has therefore a definite melting-point, thus:

TABLE 31.—MELTING-POINTS OF HYDRATES.

Hydrate.	*Melting-point.*	*Hydrate.*	*Melting-point.*
$SO_3,5H_2O$	$-25°$	$FeCl_3,6H_2O$	$+37°$
$SO_3,3H_2O$	$-39°$	$2FeCl_3,7H_2O$	$+32{\cdot}5°$
$SO_3,2H_2O$	$+8{\cdot}5°$	$2FeCl_3,5H_2O$	$+56°$
SO_3,H_2O	$+10{\cdot}4°$	$FeCl_3,2H_2O$	$+73{\cdot}5°$
$2SO_3,H_2O$	$+36°$	(compare Fig. 272, p. 786)	
(compare Fig. 135, p. 337)			

(ii) *The hydrate decomposes when heated* into a lower hydrate (or the anhydrous salt) and a solution saturated with the crystals of the new compound; the hydrate is then said to "melt in its water of crystallisation," a description that would be more accurate if applied to case (i),

where melting is complete instead of partial. In this second case the range of stability of the hydrates is determined by TRANSITION-TEMPERATURES (compare p. 12), at which alone two compounds of the series are stable in contact with the solution, thus:

TABLE 32.—TRANSITION-TEMPERATURES OF HYDRATES.

Hydrate.	*Range of Stability.*	*Hydrate.*	*Range of Stability.*
$KOH,4H_2O$.	Up to − 33°.	$CaCl_2,6H_2O$.	Up to 30°.
$KOH,2H_2O$.	−33° to + 33°.	$CaCl_2,4H_2O$.	30° to 45°.
KOH,H_2O.	+33° to +143°.	$CaCl_2,2H_2O$.	45° to 175°.
KOH.	Melts at +360°.	$CaCl_2,H_2O$.	Above 175°.

(compare Fig. 222, p. 594)

Hydrates of both types may, however, appear in the same series.

The curves showing the vapour pressure and the solubility of different hydrates always intersect one another in such a way as to show that the more stable hydrate is that which has the lower vapour pressure and the lower solubility.

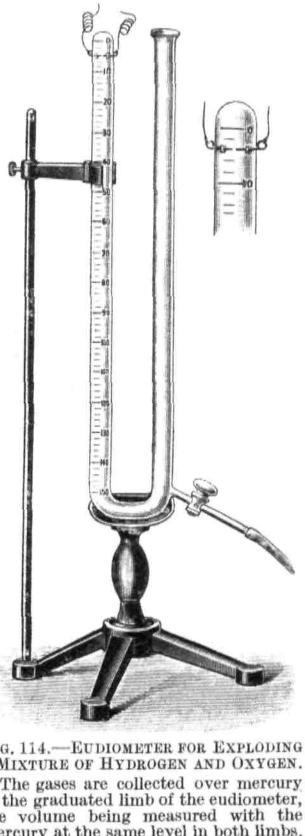


FIG. 114.—EUDIOMETER FOR EXPLODING A MIXTURE OF HYDROGEN AND OXYGEN.
The gases are collected over mercury in the graduated limb of the eudiometer, the volume being measured with the mercury at the same level in both limbs. In order to diminish the violence of the explosion, mercury is run out, so that the gases are under reduced pressure when exploded by a spark between the platinum wires of the graduated limb.

Composition of Water.

The volumetric composition of water can be determined by exploding together hydrogen and oxygen in a VOLTA'S EUDIOMETER (compare Fig. 114). If the gases are mixed in the proportion of two volumes of hydrogen to one volume of oxygen, almost complete condensation to water will take place, but the explosion is very violent unless the gases are under reduced pressure. It is therefore simpler to explode a known volume of hydrogen with an excess of oxygen, when it is found that the contraction after the explosion is 50 per cent. greater than the volume of hydrogen taken, showing that the volume of oxygen used is 50 per cent. of the volume of hydrogen.

The composition of water is sometimes deduced from the fact that the volume of hydrogen liberated at the

cathode, and the volume of oxygen liberated at the anode, when dilute sulphuric acid is electrolysed in a VOLTAMETER (Fig. 115), are in the ratio 2 : 1 approximately. This method of demonstration is, however, misleading in view of the fact that other products may be formed in addition to hydrogen and oxygen, giving rise to marked variations in the ratio of the gases (p. 259).

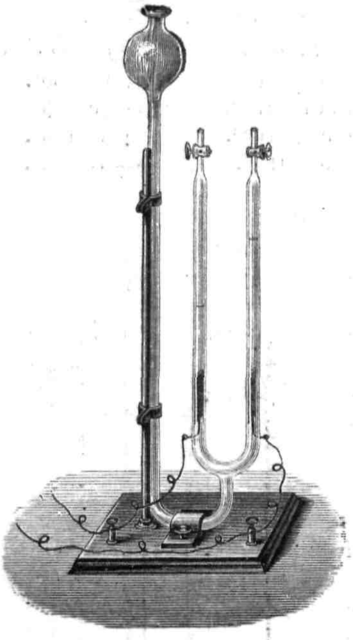


FIG. 115.—HOFMANN VOLTAMETER FOR ELECTROLYSIS OF AQUEOUS SOLUTIONS.

The methods used for determining exactly the composition of water by weight and by volume have already been described (Chapter VIII, pp. 88 and 90).

Heat of Formation and Decomposition of Water.

When 2·015 grams of hydrogen and 16 grams of oxygen at 15° are exploded together and condensed to liquid water at 15°, 68,360 calories are set free. This action is described as EXOTHERMIC, because it results in a *liberation of heat.* The amount of heat set free may be shown in a THERMO-CHEMICAL EQUATION thus :

$$2H_2 \text{ (gas)} + O_2 \text{ (gas)} = 2H_2O \text{ (liq.)} + 2 \times 68{,}360 \text{ calories.}$$

This equation is intended to show that when hydrogen and oxygen unite they give not only water, but also 68,360 calories of heat for each 18·015 grams of water produced. This quantity of heat is called the HEAT OF FORMATION of water and is sometimes written $\{H_2 \mid \frac{1}{2}O_2\} = + 68{,}360$.

In accordance with the laws of conservation of energy the decomposition of water must be an ENDOTHERMIC ACTION accompanied by an *absorption* of heat of equal magnitude :

$$2H_2O \text{ (liq.)} = 2H_2 \text{ (gas)} + O_2 \text{ (gas)} \quad - 2 \times 68{,}360 \text{ calories.}$$

Influence of Temperature on Exothermic and Endothermic Actions.

The majority of chemical changes are exothermic. Endothermic actions are not very frequent even at atmospheric temperatures and would be impossible at the absolute zero of

temperature.* When, however, the temperature is raised, endothermic actions are favoured at the expense of the exothermic actions. This is in accordance with LE CHATELIER'S THEOREM, according to which chemical changes take place in such a direction as to counteract in part the physical changes used to promote them. Thus, a rise of temperature will promote an action which absorbs heat, just as an increase of pressure will promote an action accompanied by contraction of volume. Whilst, therefore, the combination of hydrogen and oxygen at atmospheric temperatures is believed to be complete, the action at higher temperatures is not quite complete, since a small amount of unburnt hydrogen and oxygen is left in equilibrium with the water-vapour produced by combustion. Conversely, whilst water-vapour has no tendency to break up into hydrogen and oxygen at ordinary temperatures, marked decomposition takes place when water-vapour is heated very strongly.

In order to prove that this decomposition actually takes place, advantage is taken of the fact that chemical changes proceed much more slowly at low temperatures than at high temperatures, *e.g.*, in typical cases the velocity of chemical changes is doubled when the temperature is raised 10°. It is therefore possible in some instances to "fix" the products of decomposition obtained at a *high* temperature by cooling very quickly to a *low* temperature, at which recombination is either very slow or stopped completely.

Dissociation of Water.

The conditions of equilibrium between water-vapour and its component gases at different temperatures are as follows:

TABLE 33.—DISSOCIATION OF WATER-VAPOUR.

Temperature.	*Equilibrium.*	
	$2H_2 + O_2 \rightleftarrows$	$2H_2O$.
2650°	11 %	89 %
2000	1·8	98·2
1730	0·6	99·4
1200	0·02	99·98

The decomposition of water at high temperatures, which is indicated in this table, can be demonstrated by passing electric sparks through a current of steam (Fig. 116). Under these conditions, the molecules of

* Since a battery can only run in the direction of its electromotive force, the electrical energy, E, set free in a chemical change must always be positive. If the heat-energy, Q, is negative, it follows that there must be a marked temperature-coefficient dE, as indicated by the equation,

$$E - Q = T\frac{dE}{dT} \text{ (p. 194)}$$

to account for the difference of sign between E and Q.

water which have been decomposed by the heat of the spark are quenched immediately by the surrounding vapour, and this cooling is so rapid that the hydrogen and oxygen have not time to recombine before they are swept forward in the current of steam. The products of decomposition are therefore obtained as an explosive mixture when the steam is condensed.

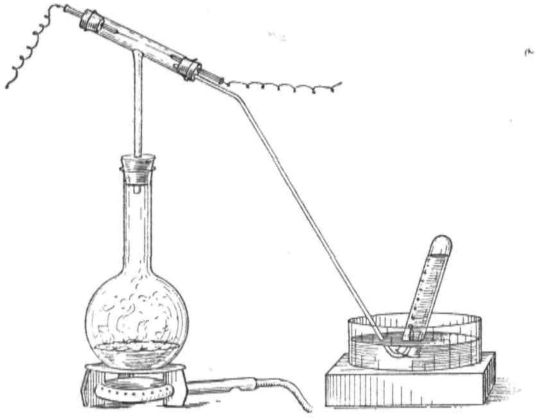


FIG. 116.—APPARATUS FOR PASSING ELECTRIC SPARKS THROUGH STEAM.

The thermal decomposition of water-vapour can also be brought about by plunging white-hot platinum under the surface of the liquid, when bubbles of inflammable gas are formed and can be collected. This thermal decomposition of water was the first chemical change to which the term DISSOCIATION was applied, but this term is now used to cover all cases of *reversible decomposition* (*e.g.*, chlorine, p. 273 ; hydrogen chloride, p. 276 ; iodine, p. 309 ; hydrogen iodide, p. 311 ; hydrogen sulphide, p. 323 ; nitric oxide, p. 404 ; nitrogen peroxide, pp. 412 and 413 ; phosphorus pentachloride, p. 434 ; carbon dioxide, p. 458 ; carbon monoxide, p. 462 ; carbonyl chloride, p. 462 ; ammonium chloride, p. 600).

The Laws of Thermo-Chemistry.

(*a*) *The Law of Constant Heat Summation.*—A simple application of the "First Law of Thermodynamics" leads to the fundamental law of thermo-chemistry, generally known as the LAW OF CONSTANT HEAT SUMMATION. In its most general form this law states that

"*The total amount of heat liberated in passing from one set of conditions to another is independent of the processes selected to bring about the change.*"

(*b*) *Influence of Temperature on Heat of Formation.*—By means of this law it is possible to calculate the influence of temperature on the heat of formation of a compound, when the specific heats of the compound and its elements are known. Thus, the heat of formation of steam at 100° can be deduced from the heat of formation of water at 15° if the specific heats of water and of its elements in the range from 15° to 100° are known, together with the latent heat of evaporation of water at 100°, as follows :

(i) The molecular heat of 2 grams of hydrogen or 32 grams of oxygen under constant pressure is about 7 calories ; the heat absorbed when heating 2 grams of hydrogen and 16 grams of oxygen from 15° to 100° is therefore $(7 + 3 \cdot 5)\ 85 = 892$ calories.

(ii) The specific heat of water from 15° to 100° may be taken as unity and its latent heat of evaporation at 100° as 537 calories. The condensation of 18 grams of steam therefore liberates $18 \times 537 = 9666$ calories and the cooling of the water from 100° to 15° liberates a further $18 \times 85 = 1530$ calories, a total of $9666 + 1530 = 11{,}196$ calories.

(iii) Since 68,360 calories are set free when 2 grams of hydrogen and 16 grams of oxygen are converted into water at 15°, it follows that the same total liberation of heat must occur in heating the gases to 100°, exploding them at 100°, and cooling the products down to 15°. If therefore the heat of formation of steam at 100° from hydrogen and oxygen at 100° be x, then

$$-892 + x + 11{,}196 = 68{,}360 \text{ calories or}$$
$$x = \mathbf{58{,}056} \text{ calories.}$$

In precisely the same way, it is possible to calculate the heat of formation of water-vapour at 0° or at 2000°, if its specific heat and those of its elements are known in the range from 100° to 0° or 100° to 2000°. The heats of formation thus deduced are, in round numbers :

58,000 calories for water-vapour at 0°, and
50,000 calories for water-vapour at 2000°.

(*c*) *Heat of Reaction.*—From this law it is also possible to calculate the HEAT OF REACTION of any chemical change by subtracting the heats of formation of the materials used from those of the products obtained, since the total heat summation must be zero in a series of operations starting and finishing with elements, thus :

(i) Formation of initial materials from their elements.
(ii) Conversion of initial materials into final products.
(iii) Decomposition of products into their elements.

Thus, the heat liberated in the conversion of carbon monoxide and water-vapour into carbon dioxide and hydrogen may be calculated from the heats of formation as follows :—

H_2	+	$\frac{1}{2}O_2$	=	H_2O (vapour)			+ 58,000	calories
C	+	$\frac{1}{2}O_2$	=	CO (gas)			+ 29,000	,,
C	+	O_2	=	CO_2 (gas)			+ 96,960	,,
H_2O	+	CO	=	H_2	+	CO_2	+ **9,960**	,,
58,000		29,000		0*		96,960		

The heat of reaction is **9,960** calories, since

$$58{,}000 \quad + \quad 29{,}000 + \mathbf{9{,}960} \quad - \quad 96{,}960 \quad = \quad 0$$

(*d*) *Heat of Combustion.*—In the same way, the heat of formation of an organic compound can be calculated from the heats of

* The heat of formation of an element in its normal condition is taken as zero.

combustion of the compound and of its elements. Thus in the case of methane or marsh gas we have

$$\begin{array}{lcllcl}
H_2 & + & \frac{1}{2}O_2 & = & H_2O \text{ (liq.)} & + \ 68{,}360 \text{ calories} \\
C & + & O_2 & = & CO_2 & + \ 96{,}960 \quad ,, \\
CH_4 & + & 2O_2 & = & CO_2 + 2H_2O \text{ (liq.)} & + \ 212{,}400 \quad ,, \\
x & & 0^* & & 96{,}960 \qquad 2 \times 68{,}360. &
\end{array}$$

According to the law of constant heat summation

$$x + 212{,}400 - 96{,}960 - 2 \times 68{,}360 = 0.$$
$$\therefore x = \mathbf{21{,}280} \text{ calories,}$$

where x is the heat of formation of methane.

(*e*) *Influence of Temperature in Balanced Actions.*—By means of the "Second Law of Thermodynamics," a quantitative relationship can be established in the case of gases between the heat liberated in a balanced action and the influence of temperature on the equilibrium. This relationship has been used very extensively to calculate, from actual measurements of equilibrium in gases, the conditions of equilibrium at temperatures too high for experimental work or too low for the attainment of equilibrium in a reasonable time. Conversely, it has been used to calculate the heat of reaction, *e.g.*, of a dissociating gas, from the variations of equilibrium with temperature.

According to NERNST'S THEOREM the equilibrium-constant varies with temperature, as shown in the equation

$$\frac{d \log_e K}{dT} = \frac{Q}{RT^2} \text{ or } \log K = \frac{Q}{4{\cdot}571\, T} + b,$$

where T is the absolute temperature,
Q is the heat of reaction at $T°$,
K is the equilibrium-constant in the mass-action equation (p. 201),
and b is a constant.

Since the heat of reaction, Q, varies with the temperature (except when the materials on both sides of the equation have the same heat-capacity), the equation usually takes the form

$$\log K = \frac{Q_0}{4{\cdot}571\, T} + a \log T + b,$$

where Q_0 is the heat of reaction reduced to $-273°$,
a is a constant depending on the specific heats, and
b is a constant depending on the substances used and produced in the action.

Chemical Properties of Water.

(*a*) *Decomposition by Heat.*—The decomposition of water by heat has been described above (p. 256).

(*b*) *Decomposition by Electrolysis.*—Water itself is a bad electrical conductor, but it becomes a good electrolyte when an acid, base, or salt

* The heat of formation of an element in its normal condition is taken as zero.

is dissolved in it. The decomposition of these conducting solutions by the electric current can be demonstrated by means of the HOFMANN VOLTAMETER, Fig. 115, p. 254. When hydrogen and oxygen are the only products of decomposition, they are formed in the ratio of two molecules of hydrogen to one molecule of oxygen and the volumes of these gases are in the ratio of two to one approximately; but when a mixture of sulphuric acid and water is used as the conducting liquid, especially with small electrodes, other products may be formed, including ozone (p. 263), hydrogen peroxide (p. 260), and persulphuric acids (p. 349). Under these conditions, the volume of oxygen set free may be much less than half the volume of hydrogen.

(c) *Decomposition by Metals.*—Many metals decompose water either in the cold (*e.g.*, sodium, potassium, magnesium-amalgam) or when heated (magnesium, iron), as described on p. 235 above.

(d) *Decomposition by Chlorine.*—Under the influence of sunlight water is decomposed reversibly by chlorine (p. 279),

$$2Cl_2 + 2H_2O \rightleftharpoons 4HCl + O_2.$$

(e) *Hydrolysis.*—It has been pointed out (p. 247) that water is formed in the neutralisation of an acid by a base. In the case of salts formed from a weak acid or base this action may be reversed in part by the addition of an excess of water, *e.g.*,

$$\underset{\text{Potassium cyanide}}{KCN} + H_2O \rightleftharpoons \underset{\text{Potassium hydroxide}}{KOH} + \underset{\text{Hydrogen cyanide}}{HCN}.$$

$$\underset{\text{Bismuth chloride}}{BiCl_3} + H_2O \rightleftharpoons \underset{\text{Bismuth oxychloride}}{BiOCl} + \underset{\text{Hydrogen chloride}}{2HCl}.$$

This decomposition by addition of water is known as HYDROLYSIS. Hydrolysis may also take place in non-metallic compounds, *e.g.*,

$$\underset{\text{Phosphorous chloride}}{PCl_3} + H_2O = \underset{\text{Phosphorous oxychloride}}{POCl} + 2HCl$$

or

$$\underset{\text{Phosphorous chloride}}{PCl_3} + 3H_2O = \underset{\text{Phosphorous acid}}{H_3PO_3} + 3HCl$$

(f) *Water as a Catalyst.*—Water is very active as a CATALYST in bringing about chemical changes which do not take place in perfectly dry materials, *e.g.*, the oxidation of hydrogen, phosphorus, sulphur, and carbon (p. 244), the combination of ammonia and hydrogen chloride, and the dissociation of ammonium chloride (p. 602). On the other hand, drying does not check the formation of ozone (p. 263), towards which water-vapour acts as an ANTICATALYST or STABILISER, increasing the stability of the ozone very considerably.

Detection and Estimation of Water.

Water can be identified by its insolubility in organic liquids such as petrol, and by its power of converting white anhydrous copper

sulphate into the blue pentahydrate, $CuSO_4,5H_2O$. More conclusive evidence is afforded by measuring its physical properties, density, freezing-point, boiling-point, etc. The purity of a sample of water may be judged in part by its colour, clearness, and taste, or quantitatively by measuring its electrical resistance, which increases with the purity of the sample (p. 43). Chemical analysis is needed, however, to detect and estimate impurities such as

(1) Metallic salts, *e.g.*, of lead and copper.
(2) Hardness, which can be estimated by adding a standard soap solution until a permanent lather is produced, or by titration of the calcium and magnesium salts in solution (p. 632).
(3) Ammonia and related compounds, which can be estimated colorimetrically by Nessler's Solution (p. 383); these compounds (with chlorides) are commonly regarded as indications of contamination by sewage.
(4) Nitrogen in the form of nitrates or nitrites, which are usually an indication of a former pollution by sewage that is no longer a source of danger, although in some localities the presence of nitrites is a sufficient reason for doubting the purity of the water.

Water is usually estimated by the loss of weight on drying, either in an oven, say at 100°, or in a desiccator over a drying agent such as sulphuric acid at atmospheric temperatures. Water can, however, be estimated directly by absorbing it by means of a drying agent such as calcium chloride, pumice stone soaked in sulphuric acid, or phosphoric oxide. The proportion of water-vapour in air can be determined either gravimetrically by absorption or by noticing the "dew-point," that is, the temperature at which the air becomes saturated with moisture and begins to deposit dew (compare Fig. 59, p. 172). The humidity of the air can also be measured by means of a wet and dry bulb thermometer, in which the cooling of the wet bulb by evaporation serves as a measure of the dryness of the air in contact with it (compare p. 367).

Hydrogen Peroxide, $H_2O_2 = 34{\cdot}015$.

Preparation.

Hydrogen peroxide is usually prepared by the action of an acid upon a peroxide, *e.g.*,

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

The insoluble barium sulphate is filtered off and any excess of sulphuric acid removed by the addition of barium carbonate. The clear filtrate may be concentrated by evaporating under reduced pressure and the anhydrous peroxide can finally be distilled. The concentrated solutions are stored in bottles lined with paraffin wax, in order to minimise

decomposition resulting from the catalytic action of alkali from the glass, and can be stabilised by the addition of acetanilide, $C_6H_5 \cdot NH \cdot CO \cdot CH_3$, a mere trace of which is sufficient to enable the peroxide to retain its strength even in tropical climates.

Physical Properties of Hydrogen Peroxide.

Anhydrous hydrogen peroxide is a liquid of density 1·46, which solidifies to crystals which melt at − 1·7°.

Chemical Properties of Hydrogen Peroxide.

(*a*) *Decomposition and Dissociation.*—Hydrogen peroxide is an exothermic compound,

$$H_2 \text{ (gas)} + O_2 \text{ (gas)} = H_2O_2 \text{ (soln.)} + 45{,}300 \text{ cal.}$$

It is, however, less exothermic than water, and a considerable amount of heat is, therefore, set free when it decomposes into water and oxygen :

$$\underset{2\times 45{,}300}{2H_2O_2} = \underset{2\times 68{,}360.}{2H_2O} + O_2 + 2\times 23{,}060 \text{ cal.}$$

At atmospheric temperatures hydrogen peroxide decomposes slowly, but completely, according to the above equation. The decomposition is accelerated by alkalies, by contact with metals such as platinum, and with finely-divided solids such as manganese dioxide, which cause a rapid liberation of oxygen gas. The decomposition of hydrogen peroxide appears, however, to be checked at very high temperatures, since the peroxide can be detected amongst the products of combustion of hydrogen and oxygen by directing the flame against ice, or better against a block of solid carbon dioxide, in order to chill it. The formation of hydrogen peroxide under these conditions may be explained (i) as a reversal at high temperatures of the exothermic decomposition into water and oxygen shown in the preceding equation, or (ii) by the formation of hydrogen peroxide as the primary product of combination of a single molecule of hydrogen with a single molecule of oxygen,

$$H_2 + O_2 = H_2O_2,$$

in which case water would be a secondary product.

(*b*) *Hydrogen Peroxide as an Oxidising Agent.*—Hydrogen peroxide is a powerful oxidising agent. It liberates iodine from potassium iodide,

$$2KI + H_2O_2 = I_2 + 2KOH,$$

oxidises ferrous salts to ferric salts,

$$2FeSO_4 + H_2SO_4 + H_2O_2 = Fe_2(SO_4)_3 + 2H_2O,$$

and sulphides to sulphates, *e.g.*,

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O.$$

It converts sulphuric acid into persulphuric acids, *e.g.*,

$$H_2O_2 + H_2SO_4 \rightleftharpoons H_2SO_5 + H_2O,$$

and chromic anhydride, CrO_3, into a perchromic acid, $HCrO_5$, which can be separated in the form of crystalline salts, *e.g.*, $(NH_4)CrO_5,H_2O_2$ and $KCrO_5,H_2O_2$, which have been formulated as containing HYDROGEN PEROXIDE OF CRYSTALLISATION.

Hydrogen peroxide and potassium permanganate, which are both very powerful oxidising agents, possess the remarkable property of reducing one another with liberation of oxygen gas,

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

In the same way, silver oxide and hydrogen peroxide reduce one another,

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2.$$

In these actions the decomposition appears to be caused by the tendency of oxygen atoms to unite with one another to form oxygen molecules.

On account of its oxidising action hydrogen peroxide is a powerful bleaching agent and is used in bleaching straw, textiles, and hair, which would be injured by other bleaching agents. It is also of value as an antiseptic.

(*c*) *Acid Properties.*—Hydrogen peroxide, even when freed from sulphuric acid by distillation, has an acid reaction, the neutral character of water being converted into acidity by the additional atom of oxygen. Its acid qualities are also shown by its power of combining or interacting with alkalies. Thus, when sodium hydroxide is added to hydrogen peroxide, alcohol precipitates from the solution a pure hydrated sodium peroxide, $Na_2O_2,8H_2O$:

$$2NaOH + H_2O_2 \rightleftharpoons \underset{\text{Sodium peroxide}}{Na_2O_2} + 2H_2O.$$

Again, when baryta is added to aqueous hydrogen peroxide, a crystalline barium peroxide, $BaO_2,8H_2O$, is thrown down:

$$Ba(OH)_2 + H_2O_2 = \underset{\text{Barium peroxide}}{BaO_2} + 2H_2O;$$

this precipitated peroxide can be used with advantage in the manufacture of pure hydrogen peroxide from the crude hydrogen peroxide obtained by the action of hydrochloric acid on commercial barium peroxide.

These metallic peroxides can be considered as salts of hydrogen peroxide. It should, however, be noted that whilst sulphuric acid, $SO_2(OH)_2$, is dibasic, the permonosulphuric acid, $HO{\cdot}O{\cdot}SO_2{\cdot}OH$, shown in a previous equation (p. 261), is only monobasic, the acid properties of the peroxide group $-O{\cdot}OH$ being small compared with those of the sulphonic group $-SO_2{\cdot}OH$.

Detection and Estimation of Hydrogen Peroxide.

Hydrogen peroxide can be detected by its oxidising action on potassium iodide, especially in presence of starch, which forms a deep

blue compound with the liberated iodine; but this test is not conclusive, as it is given by many other oxidising agents. Hydrogen peroxide is, however, reduced only very slowly by ferrous sulphate; it can therefore be detected, even in presence of other oxidising agents, by oxidation of potassium iodide after adding ferrous sulphate to reduce all other oxidisers. The oxidation of chromic acid to perchromic acid can also be used as a sensitive test for hydrogen peroxide by adding potassium dichromate, dilute sulphuric acid, and ether; when hydrogen peroxide is present, the ether extracts a blue perchromic acid from the dark solution. With chromic acid and aniline, hydrogen peroxide gives a violet coloration to ether.

Hydrogen peroxide may be estimated by adding potassium iodide, when iodine is liberated slowly and can be estimated colorimetrically or by titration. It can also be estimated in presence of other oxidising agents by direct titration with potassium permanganate, which is reduced by hydrogen peroxide, but is not affected by other oxidising agents.

OZONE. $O_3 = 48$ (exactly).

Formation of Ozone.

A very active variety of oxygen is produced by the action of an electric discharge in air or oxygen. On account of its pungent odour, it is known as OZONE (Greek ὄζω, I smell). The production of ozone was first noticed during the working of a frictional electrical machine. It is also formed in small quantities when oxygen is set free by the following methods:—

(i) *By Electrolysis*; the oxygen may contain as much as 28 per cent. of ozone when small platinum electrodes and high current-densities are used.

(ii) *By the action of Fluorine on Water at* 0°: the oxygen prepared in this way contains about 12 per cent. of ozone.

(ii) *By the decomposition of Hydrogen Peroxide, e.g.*, when barium peroxide is acted upon by strong sulphuric acid.

Preparation of Ozone.

Ozone is best prepared by the action of a SILENT DISCHARGE on air or oxygen. This discharge differs from the ordinary spark discharge in that one or two layers of an insulating material, such as glass or mica, are inserted between the metallic terminals. The formation of large sparks or of an electric arc (which tend to produce oxides of nitrogen) is thereby prevented, and the discharge is restricted to a series of minute sparks oscillating to and fro between the insulating surfaces. A simple form of ozoniser is shown in Fig. 117. Ozone is also formed during the smouldering of phosphorus and can be produced by the action of ultra-violet light on air or oxygen.

The formation of ozone from oxygen is a strongly endothermic action,

$$3O_2 = 2O_3 - 2 \times 34{,}000 \text{ calories.}$$

The conversion of oxygen into ozone is therefore favoured by rise of temperature just like the endothermic decomposition of water into hydrogen and oxygen. It is therefore not surprising that some of the dark lines in the solar spectrum have been identified as due to ozone in the sun's atmosphere. At ordinary temperatures, however, ozone tends to decompose completely, and, as it is even less stable than a mixture of hydrogen and oxygen, the "quenching" of the heated molecules must be very rapid and efficient in order to retain the ozone which is produced at high temperatures. It is for this reason that the minute sparks of the silent discharge are better agents for producing

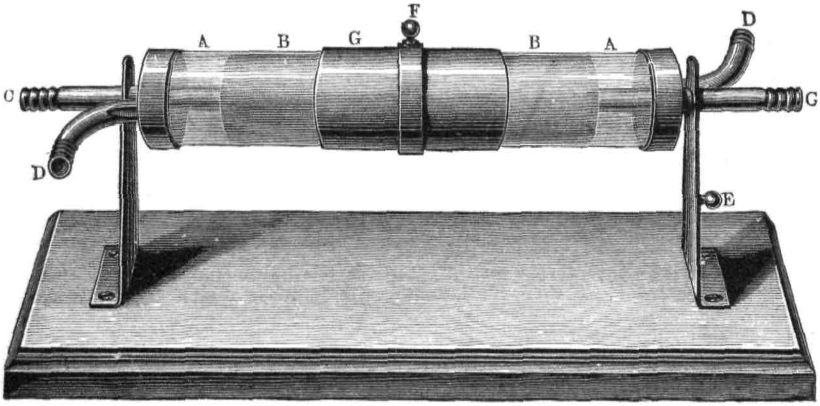


FIG. 117.—SIMPLE OZONISER.

The discharge from an induction coil is led through *E* and *F* to a water-cooled iron cylinder, *B*, and to a cylinder, *G*, of tin-foil, separated from it by a glass tube, *AA*. Air or oxygen is led in and out of the apparatus at *DD*, and is ozonised in its passage through the narrow space between the cylinder, *BB*, and the glass tube carrying the tin-foil, *G*.

ozone than a heavier discharge; indeed any discharge which heated the whole current of gas to 200° would be useless for making ozone, since ozone is decomposed very rapidly and completely at this temperature.

Physical Properties of Ozone.

When ozone is prepared by the action of the silent electric discharge on oxygen, about 14 per cent. of the oxygen may be converted into ozone at 0°. When this OZONISED OXYGEN is cooled by means of liquid air, the ozone condenses to a deep blue liquid, boiling at − 119°, and, like liquid oxygen, strongly magnetic; but the blue gas obtained by the evaporation of liquid ozone is liable to explode violently when the temperature is raised, or in the presence of the smallest trace of organic matter.

Ozone is soluble in water and imparts to it a disagreeable taste and smell. Water which has been sterilised by means of ozone must therefore be exposed to the air in order to render it palatable again. For similar reasons ozone cannot be used alone for bleaching flour.

The less volatile portions of liquid ozone give a denser gas of higher chemical activity, which is decomposed by washing twice with caustic potash or with sulphuric acid; this less volatile compound has been described as OXOZONE and the formula O_4 has been proposed for it.

Chemical Properties of Ozone.

Ozone is an extremely powerful oxidising agent.

(*a*) It liberates iodine from potassium iodide according to the equation

$$2KI + O_3 + H_2O = I_2 + 2KOH + O_2.$$

The blue colour produced by the iodine in presence of starch forms a very sensitive test for ozone. This oxidation is also used for the quantitative estimation of ozone, since the iodine and the caustic potash may both be estimated by titration; the titration of the iodine is, however, impossible in the presence of oxides of nitrogen. In this action there is no change in the volume of the gas, since the oxidation is effected entirely by the extra atom of oxygen in ozone.

(*b*) Ozone, even in small quantities, will oxidise mercury in such a way that it becomes very dirty and clings to the sides of the bottle containing it. It also oxidises sulphides to sulphates, ferrocyanides to ferricyanides, and manganous to manganic compounds.

(*c*) Ozone will oxidise many organic compounds, *e.g.*, it will bleach indigo which has been dissolved in fuming sulphuric acid and then diluted with water. Rubber joints cannot be used for ozone because the gas eats through them in the course of two or three minutes; it has, however, no action on paraffin wax. The physiological effects of ozone are disagreeable except at extreme dilutions; it attacks the mucous membrane of the throat and in many cases is found to produce headache. Ozone has found an extensive application in purifying air, *e.g.*, in underground railways; the ozone of sea-air is, however, probably a myth, founded upon the presence of salt-spray in the air, and perhaps on the odour of decaying sea-weed.

(*d*) Ozone is absorbed as a whole by turpentine, apparently forming an "addition compound" which is described as an OZONIDE.

(*e*) Ozone may be distinguished from hydrogen peroxide and oxides of nitrogen by bubbling the gas through a solution of potassium permanganate, which destroys the two latter compounds. Conversely, oxides of nitrogen may be distinguished from ozone and hydrogen peroxide by destroying them either by gentle heat or by a catalyst such as manganese dioxide, and then absorbing the oxides of nitrogen in an alkali. Finally, the vapour of hydrogen peroxide may be distin-

guished by its power of reducing ferric ferricyanide to Prussian blue (p. 790).

Decomposition of Ozone.

Ozone is a very unstable gas; it decomposes slowly at atmospheric temperatures and rapidly at 200°. The decomposition is greatly accelerated by oxides of nitrogen, but is retarded by the presence of water; thus, Shenstone found that dry ozone at 0° decomposed thirty times as rapidly as the damp gas at 26·4°. It is therefore possible that the explosive character of ozone evaporated from the liquid (p. 264) is due to the complete drying which it receives under these conditions.

The decomposition of ozone is very rapid in the presence of finely-divided metals such as platinum black, or of oxides such as silver oxide and manganese dioxide, all of which remain unaltered at the end of the action.

Formula of Ozone.

(*a*) The formula of ozone was determined by Soret in 1866 by comparing the expansion when ozone was decomposed by heat with the contraction when it was absorbed by turpentine.

Turpentine was introduced into 230 c.c. of ozonised oxygen, contained in a flask with a long graduated neck, which dipped into water; the decrease in volume produced by the complete absorption of the ozone was observed. A similar flask containing 230 c.c. of the same sample of ozonised oxygen was heated with a flame in order to decompose the ozone; the increase in volume, after cooling to the original temperature, was noted. The results of three experiments were :—

Decrease in volume due to absorption of ozone = *V*.	Increase in volume due to decomposition of the ozone = *v*.	$\frac{V}{v}$.
6·7 c.c.	3·30 c.c.	2·03
6·9	3·45	2·00
5·7	2·72	2·10

The expansion produced by the decomposition of ozone into oxygen was equal to half the volume of the ozone. Its molecular weight is therefore 50 per cent. greater than that of oxygen, as indicated by the formula O_3, and the equation

$$\underset{\substack{\text{Oxygen} \\ 3\ vols.}}{3O_2} \rightleftarrows \underset{\substack{\text{Ozone} \\ 2\ vols.}}{2O_3}$$

(*b*) The formula of ozone was also deduced by Soret in 1868 from its density as determined by comparing its rate of diffusion with that of chlorine.

The usual method of allowing the gas to diffuse through a porous partition could not be used, as ozone is rapidly destroyed by contact with porous materials. Soret therefore measured in a series of samples of ozonised oxygen

the proportion of ozone which passed in the course of 45 minutes through a cylindrical hole (5 mm. in diameter) from a cylinder of 250 c.c. capacity into a similar cylinder containing oxygen only. A series of tests was also made with chlorine. The proportions in the two cases were 0·2708 and 0·2270. According to Graham's Law of Diffusion, taking the density of chlorine as 35·46 (oxygen = 16) and that of ozone as x,

$$\sqrt{x} : \sqrt{35 \cdot 46} = 0 \cdot 2270 : 0 \cdot 2708, \text{ and } x = 24 \cdot 9.$$

The density of ozone is therefore about 25 and its molecular weight is about 50, corresponding with the formula $O_3 = 48$.

(*c*) Ladenburg in 1901 determined the density of ozone directly, by weighing ozonised oxygen of known concentration against pure oxygen, and confirmed Soret's values for the density and molecular weight of the gas.

A glass sphere, when filled with ozonised oxygen, was found to weigh 0·0075 gram more than when filled with pure oxygen. On admitting turpentine, 9·7304 grams of turpentine of density 0·8692, *i.e.*, 11·20 c.c., were drawn in to take the place of the ozone which it absorbed. The weight of an equal volume of oxygen at 13·3° and 748·6 mm. pressure is

$$11 \cdot 20 \times \frac{1 \cdot 429}{1000} \times \frac{748 \cdot 6}{760} \times \frac{273}{286 \cdot 3} = 0 \cdot 0150 \text{ gram.}$$

The weight of the ozone was therefore

$$0 \cdot 0150 + 0 \cdot 0075 = 0 \cdot 0225 \text{ gram,}$$

and its density, taking the density of oxygen as 16, is

$$16 \times \frac{0 \cdot 0225}{0 \cdot 0150} = 24 \cdot 0.$$

These experiments showed that ozone was 50 per cent. heavier than oxygen, so that its formula must be O_3.

CHAPTER XXIII

17. CHLORINE. Cl = 35·46

Occurrence of Chlorine.

Chlorine is present in igneous rocks to the extent of $\frac{1}{16}$ per cent. only, probably in the form of APATITE, $Ca_5(PO_4)_3[F,Cl]$, a phosphate-fluoride, in which a part of the fluorine may be replaced vicariously by chlorine. When these rocks are decomposed by the action of air and water, chlorine is washed out, so that the proportion in sedimentary rocks is only $\frac{1}{50}$ per cent. Since all the commoner chlorides are soluble in water, they are carried down by the rivers to the sea, where they have accumulated to such an extent that the chlorine alone forms 2 per cent. by weight of the ocean. This chlorine is present mainly in the form of common salt, which if crystallised out would form a layer more than 100 feet in thickness over the surface of the earth, the total bulk of SEA SALT being estimated at five million cubic miles. In inland lakes, such as the Dead Sea, the concentration of the soluble salts may proceed to a point in which large quantities of common salt are crystallised out, giving rise ultimately to deposits of ROCK SALT.

COMMON SALT, or **sodium chloride,** NaCl, in the form either of sea salt or rock salt, is the universal source of chlorine. The mother-liquors from which the salt crystallises contain **potassium chloride,** KCl, and **magnesium chloride,** $MgCl_2$; these are therefore found in the upper layers of salt beds, as at Stassfurt and in Alsace, where the mother-liquors as well as the common salt have crystallised out, and then been protected from dissolution, *e.g.* by a layer of clay. Chlorine is also present in volcanic gases as sal-ammoniac or **ammonium chloride,** NH_4Cl, whilst insoluble **silver chloride,** AgCl, is found as a mineral as HORN-SILVER.

Chlorine as a Product of Oxidation of Hydrogen Chloride.

Chlorine was discovered by Scheele in 1774 as a product of the oxidising action on muriatic or hydrochloric acid (prepared by the action of oil of vitriol on common salt, p. 49) of a mineral which was then called MANGANESE, but which is now generally known as PYROLUSITE or manganese dioxide. In this action the hydrogen of the acid is removed by oxidation to water, and the chlorine is set free,

$$4HCl + O_2 = 2H_2O + 2Cl_2 ;$$

but when Berthollet, in 1785, discovered that chlorine-water on exposure to sunlight liberated oxygen and reverted to hydrochloric acid (the converse of the preceding action) he concluded that chlorine had been decomposed into muriatic acid and oxygen, and was therefore an oxide of muriatic acid, to which he gave the name OXYMURIATIC GAS. The idea that chlorine is an element was due to Davy, who was unable to separate oxygen from it even by an electric arc burning between carbon poles, and therefore proposed in 1810 to call the gas CHLORINE because of its green colour (Greek χλωρός, green) instead of by a name which implied the presence of oxygen in it.

Preparation of Chlorine.

Chlorine is generally prepared either by the oxidation of hydrochloric acid or by the electrolysis of a metallic chloride, usually common salt.

(*a*) *Oxidation of Hydrogen Chloride by Peroxides.*

$$MnO_2 + 4HCl\ (hot) = Cl_2 + MnCl_2 + 2H_2O$$
$$MnO_2 + 2NaCl + 3H_2SO_4 = Cl_2 + MnSO_4 + 2NaHSO_4 + 2H_2O$$
$$2KMnO_4 + 8HCl\ (cold) = 3Cl_2 + 2KCl + 2MnO_2 + 4H_2O$$

Chlorine was manufactured until quite recently from hydrochloric acid and manganese dioxide. The first action is perhaps the formation of a manganese tetrachloride, from which the dioxide is precipitated by dilution with water, but which is decomposed by heat with liberation of chlorine and formation of a dichloride:

$$MnO_2 + 4HCl \rightleftharpoons MnCl_4 + 2H_2O$$
$$MnCl_4 \longrightarrow MnCl_2 + Cl_2;$$

the highest chloride actually separated from the solution is, however, a double salt of manganese trichloride, $MnCl_3$. In the same way, the first action of concentrated hydrochloric acid on lead peroxide at 0° is to produce plumbic chloride, $PbCl_4$ (p. 697), which yields the dioxide again when diluted with water, but decomposes at the ordinary atmospheric temperature, giving plumbous chloride, $PbCl_2$, and chlorine:

$$PbO_2 + 4HCl \rightleftharpoons PbCl_4 + 2H_2O.$$
$$PbCl_4 = PbCl_2 + Cl_2.$$

The spent liquor containing the manganous chloride was mixed with an excess of milk of lime, in order to precipitate manganous hydroxide,

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2,$$

which was oxidised by blowing steam and air through the mixture, when oxygen was absorbed and calcium manganite, $CaMnO_3$ or CaO,MnO_2, was formed:

$$2Mn(OH)_2 + 2Ca(OH)_2 + O_2 = 2CaMnO_3 + 4H_2O.$$

This method of recovering the manganese and rendering it available for further use is known as the WELDON RECOVERY PROCESS. The

sediment, which consists mainly of calcium manganite, $CaMnO_3$, and manganous manganite, $MnMnO_3$, is known as WELDON MUD, and can be used instead of fresh manganese dioxide for the preparation of chlorine. It should be noted, as an example of the acidifying qualities of oxygen, that in the presence of *acids* manganese tends to come down in the scale of oxidation to the strongly *basic* manganous oxide, MnO ; but when liberated from its salts it is oxidised to the *neutral* or *feebly acid* manganese dioxide, MnO_2 ; and, finally, fusion with *alkalies* in air converts it into manganates derived from the *acid* oxide, MnO_3.

Scheele's method of preparing chlorine can be modified by using a mixture of sulphuric acid and salt instead of hydrochloric acid, but in this case the action is incomplete and the yield of chlorine poor ; moreover, twice as much sulphuric acid is required, the whole of the sodium sulphate is wasted, and the recovery process would be complicated by the presence of sodium salts.

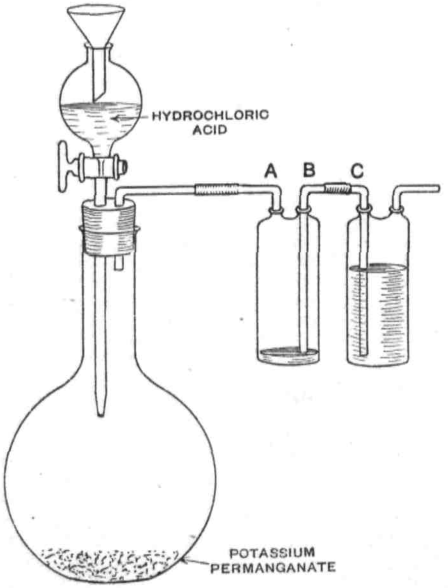


FIG. 118.—APPARATUS FOR PREPARING CHLORINE.

Small quantities of chlorine may be prepared very conveniently by allowing hydrochloric acid to flow from a dropping funnel on to potassium permanganate contained in a flask provided with a tube for the escape of the gas as in Fig. 118. The action takes place in the cold, and each drop of acid liberates immediately a corresponding quantity of chlorine ; when the flow of acid ceases the action stops almost at once. Two small wash-bottles (arranged as a VOLHARD GAS-TRAP so that the contents cannot be drawn back into the flask) can be used for washing or drying the gas, or larger bottles arranged in the same way can be used for making chlorine-water (see below). When rather larger quantities of chlorine are required, a large bottle can be used, containing two or three pounds of potassium permanganate, and the acid can be allowed to siphon over into a cylindrical separating funnel from a "Winchester quart" bottle.

(*b*) *Action of Oxygen on Hydrogen Chloride.*—In the Deacon process the exothermic oxidation of gaseous hydrogen chloride by oxygen was made use of for the commercial preparation of chlorine.

$$2HCl + \tfrac{1}{2}O_2 \rightleftharpoons Cl_2 + H_2O \text{ (vapour)} + 14{,}000 \text{ calories}$$

A mixture of hydrogen chloride and air, previously heated to 500°, was passed over porous materials impregnated with cupric chloride, and kept at the same temperature ; about 60 per cent. of the hydrogen chloride was converted into chlorine, and the rest removed by passing the gases through water. The cupric chloride remains unchanged at the end of the action and may be regarded as a catalyst ; other copper salts may be used, as well as salts of other metals, but cupric chloride is the most efficient. The oxidation is a reversible change in which the endothermic back-action becomes more and more pronounced as the temperature is raised. At low temperatures (say 300°) the oxidation would be virtually complete, but is too slow to be of any practical value. As the temperature rises, the action becomes more rapid but less complete. When the best available catalyst is used, the oxidation must still be carried out at so high a temperature that little more than half of the material is oxidised.

The Deacon process resembles in many respects the exothermic oxidation of sulphur dioxide to sulphur trioxide (p. 333), where again, when ferric oxide is used as a catalyst, only about two-thirds of the material can be oxidised ; with platinised asbestos, however, the sulphur dioxide can be oxidised rapidly at a much lower temperature and thus converted almost completely into the trioxide. No catalyst of similar high efficiency has been discovered for oxidising hydrogen chloride to chlorine, nor is this of any great importance in view of the rapid progress which has been made by the electrolytic process of manufacture, in which chlorine is prepared directly from salt without even making hydrochloric acid from it.

It has been suggested that the mechanism of the action of the catalyst in the Deacon process is as follows :—

(i) Cupric chloride decomposes into cuprous chloride and chlorine,

$$2CuCl_2 = Cu_2Cl_2 + Cl_2 ;$$

(ii) cuprous chloride combines with oxygen to form an oxychloride,

$$2Cu_2Cl_2 + O_2 = 2Cu_2OCl_2, \ \textit{i.e.,} \ O\begin{cases} Cu{\cdot}Cl \\ Cu{\cdot}Cl \end{cases} ;$$

(iii) this oxychloride is acted on by hydrogen chloride, giving water and regenerating the cupric chloride,

$$Cu_2OCl_2 + 2HCl = 2CuCl_2 + H_2O.$$

(*c*) *Electrolysis of Chlorides.*—Large quantities of chlorine are prepared by the electrolysis of brine :

$$NaCl = \overset{+}{Na} + \overset{-}{Cl} \text{ and } 2Cl = Cl_2.$$

Sodium is liberated at the cathode and acts upon the water, yielding caustic soda and hydrogen, whilst chlorine is liberated in the gaseous state at an anode of graphite or of magnetic oxide of iron, which is not attacked by it. In this process it is essential to keep apart the products

formed at the anode and at the cathode; the apparatus used for this purpose is described under "soda" (p. 565).

Chlorine can also be prepared by the electrolysis of a strong solution of hydrogen chloride,

$$2HCl = H_2 + Cl_2,$$

and has been manufactured commercially by the electrolysis of zinc chloride,

$$ZnCl_2 = Zn + Cl_2.$$

Very pure chlorine can be obtained by the electrolysis of pure fused silver chloride,

$$2AgCl = 2Ag + Cl_2.$$

The silver chloride is melted in a U-tube of hard glass protected by asbestos, Fig. 119. The current passes from a graphite anode, at which the chlorine is liberated, to a carbon cathode, at which silver is deposited. The deposited silver tends to grow out in crystals from one electrode to the other, but the bridge of silver crystals can be melted and broken down by passing a strong current for a short time.

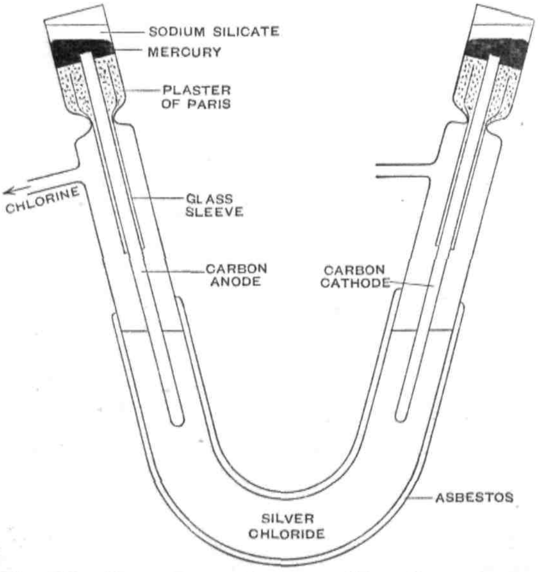


FIG. 119.—APPARATUS FOR PREPARING PURE CHLORINE BY ELECTROLYSIS OF FUSED SILVER CHLORIDE. (Mellor and Russell.)

(*d*) *Methods of Collecting and Storing Chlorine.*—Chlorine cannot be collected over cold water, in which it is freely soluble, nor over mercury, which is attacked at once by chlorine; it may be collected over hot water or brine (in which it is much less soluble) or by displacement of air. In commercial practice, chlorine is dried by the action of strong sulphuric acid, liquefied by pressure, and stored in large iron cylinders or drums, which are not attacked by the dry gas.

Chlorine is also stored and handled in combination with lime in the form of BLEACHING POWDER (p. 633),

$$Ca(OH)_2 + Cl_2 = CaOCl_2 + H_2O$$

The chlorine can be liberated again by the action of acid,

$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2,$$

but hypochlorous acid is also produced,

$$CaOCl_2 + HCl = CaCl_2 + HOCl,$$

and in the presence of cobalt salts oxygen is liberated (p. 230) instead of chlorine.

Physical Properties of Chlorine.

Chlorine is a greenish-yellow gas with a pungent odour and very corrosive properties.

(*a*) *Density*.—Its density at 0° and 760 mm. is appreciably higher than that required for the formula Cl_2. The theoretical value is maintained from 240° up to 1200°. Above this temperature dissociation takes place, the calculated proportions of the diatomic and monatomic molecules being as follows :

TABLE 34.—DISSOCIATION OF CHLORINE.

	Cl_2	$\rightleftharpoons$	2Cl.
At 1667°	99%		1 %
At 1997°	90		10
At 2337°	50		50

(*b*) *Liquefaction*.—At atmospheric temperatures chlorine can be condensed to a yellow liquid under a pressure of 4 or 5 atmospheres. Liquid chlorine is a non-conductor of electricity, and solutions of inorganic substances, such as hydrogen chloride, in liquid chlorine are also non-conductors.

The liquid freezes at − 102° and boils at − 34°, the density of the liquid at the boiling-point being 1·568. The critical temperature is 146° and the critical pressure 93·5 atmospheres.

(*c*) *Solubility*.—Water dissolves 4·6 volumes of chlorine at 0° and half this amount at 20° ; the solution is known as CHLORINE-WATER.

Chlorine-water can be prepared by bubbling the gas through water in two bottles arranged in the same way as the Volhard gas-trap shown in Fig. 118 (p. 270). The tube *A* is connected to the chlorine apparatus ; the tubes *B* and *C* reach to the bottom of the bottles ; some chlorine is dissolved at the surface of the water in the first bottle, but most of it is absorbed by passing through the water in the second bottle. This apparatus is arranged so that there is no danger of the water sucking back into the chlorine-generator.

When the saturated solution is cooled, CHLORINE HYDRATE, $Cl_2,8H_2O$, crystallises out in the form of regular octahedra. At temperatures above 29°, however, the solid hydrate is no longer stable, and chlorine and water (under pressure) form two liquid layers, just as the

hydrate of sulphur dioxide and water, $SO_2,7H_2O$ (p. 330), breaks up and forms two layers above 12°. Chlorine hydrate was used by Faraday in the preparation of liquid chlorine. The hydrate was placed in the limb *a* of a bent tube, *b* (compare Fig. 120)*, and the limb *c* was cooled by a freezing mixture; on warming the hydrate, chlorine was set free and condensed as a liquid in the limb *c*.

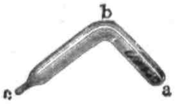


FIG. 120.—BENT TUBE FOR LIQUEFACTION OF CHLORINE.

Chemical Properties of Chlorine. Comparison of Chlorine and Oxygen.

(*a*) *Chlorine and Oxygen as Supporters of Combustion.*—In its general properties, chlorine shows a resemblance to oxygen, which is sometimes overlooked on account of the different valency of the two elements and the dissimilar formulæ of their compounds. Chlorine and oxygen, however, stand out from the other elements as gaseous SUPPORTERS OF COMBUSTION in which various inflammable substances, including a number of metals, will burn, whilst hydrogen will explode violently when mixed either with oxygen or with chlorine. Perhaps on account of their close resemblance, chlorine and oxygen do not unite directly with one another, and their compounds when prepared indirectly are unstable substances.

(*b*) *Comparison of Chlorides and Oxides.*—Chlorine possesses neither the acid-producing nor the base-producing qualities of oxygen. Thus, where oxygen converts metals into bases and non-metals into acids, chlorine is a HALOGEN (p. 65) which converts the metals directly into salts, whilst the chlorides of the non-metals are usually neutral oils. The chlorides resemble the oxides, however, in that DOUBLE CHLORIDES (compare the oxy-salts, *e.g.*, $MgO + SO_3 = MgSO_4$) often possess more distinct saline qualities than the simple chlorides from which they are derived; thus, stannic chloride, $SnCl_4$, which is an oil, unites with potassium chloride, KCl, to form a double salt, **potassium stannichloride,** K_2SnCl_6 (p. 688), which is crystalline and salt-like in all its properties.

(*c*) *Hydrogen Chloride and Water.*—The contrast between the hydrides of chlorine and oxygen appears at first sight to be even more pronounced than that between the metallic chlorides and the metallic oxides, since water is by definition a neutral compound, whilst hydrogen chloride is commonly regarded as strongly acid. In view, however, of the fact that anhydrous hydrogen chloride has no action on metals (except aluminium) or on chalk, and acquires acid qualities only when mixed with water, the contrast between the two compounds is perhaps less complete than is commonly supposed.

* Faraday does not give a figure to illustrate his apparatus.

Addition and Substitution of Chlorine.

In general, it may be said that chlorine forms two types of derivatives, namely,

(*a*) *Addition-compounds* in which chlorine combines directly with non-metals, with metals, or with UNSATURATED COMPOUNDS in which the combining power of the constituent elements is only partially satisfied, leaving a residue of combining power which can be satisfied by union with chlorine or other elements, *e.g.*,

$$CO + Cl_2 \rightleftarrows COCl_2 \quad \text{or} \quad PCl_3 + Cl_2 \rightleftarrows PCl_5.$$

Some of these addition-compounds undergo dissociation (p. 256) and break down again when heated.

(*b*) *Substitution derivatives*, in which chlorine displaces hydrogen, oxygen, sulphur, etc., from SATURATED COMPOUNDS in which the combining powers of the constituent elements are so fully satisfied that combination with chlorine can only be effected by releasing some other element, *e.g.*,

$$CH_4 + Cl_2 = CH_3Cl + HCl,$$
$$2CaO + 2Cl_2 = 2CaCl_2 + O_2$$
$$HgS + Cl_2 = HgCl_2 + S.$$

(*c*) Chlorides can also be formed by substituting metals for hydrogen in hydrogen chloride, *e.g.*,

$$Zn + 2HCl = ZnCl_2 + H_2,$$

as well as by DOUBLE DECOMPOSITION, *i.e.*, by the interaction of two compounds, both of which are decomposed in the process, *e.g.*,

$$ZnO + 2HCl = ZnCl_2 + H_2O.$$

Combination of Chlorine with Hydrogen.

(*a*) Hydrogen and chlorine combine slowly when exposed to diffused daylight. On exposure to direct sunlight, violent explosion usually occurs, but a mixture of *dry* chlorine and *dry* hydrogen does not explode in sunlight, and in one experiment 25 per cent. of such a mixture remained uncombined after four days' exposure to sunlight. Explosion also occurs when the mixed gases are heated to about 250° in a closed vessel or when a current of the gas is heated to about 440°.

The combination of hydrogen and chlorine has been used to measure the intensity of light in Bunsen and Roscoe's ACTINOMETER. The interaction is preceded by a PERIOD OF INDUCTION, during which no marked combination occurs. This has been shown to be due to the presence of impurities, such as ammonia, in the water over which the gases are confined.

(*b*) The great affinity of chlorine for hydrogen may be illustrated by the following experiments:

(i) A burning jet of hydrogen will continue to burn when thrust into a jar of chlorine, with the production of hydrogen chloride;

(ii) a lighted candle will burn in chlorine with the liberation of soot and the formation of hydrogen chloride ;

(iii) a piece of paper moistened with turpentine, $C_{10}H_{16}$, will ignite spontaneously in chlorine and continue to burn with a smoky flame.

In (ii) and (iii) the smokiness of the flame is due to the fact that the chlorine unites only with the hydrogen and not with the carbon, which is therefore deposited in the form of soot.

(c) The burning of hydrogen in chlorine is an exothermic change, although the liberation of heat is less than when hydrogen is burnt in oxygen ; in presence of water, which has a great affinity for hydrogen chloride, this order is reversed, since the heat of formation of 2HCl aq. is greater than that of H_2O liq. (compare p. 279).

$$H_2\,(gas) + Cl_2\,(gas) = 2HCl\,(gas) + 44{,}000 \text{ calories.}$$
$$H_2\,(gas) + Cl_2\,(gas) + aq. = 2HCl,\,aq. + 78{,}800 \text{ calories.}$$
$$H_2\,(gas) + \tfrac{1}{2}O_2\,(gas) = H_2O\,(liq.) + 68{,}360 \text{ calories.}$$

Reversal of the exothermic action is only slight even at very high temperatures, as may be seen from the following table.

TABLE 35.—DISSOCIATION OF HYDROGEN CHLORIDE.

	$H_2 + Cl_2$	$\rightleftharpoons$ 2HCl.	
At 1227°	0·06%	99·94%	calculated.
At 1727°	0·4	99·6	calculated.
At 2227°	1·3	98·7	calculated.
At 1537°	0·27	99·73	observed.

The reverse action can, however, be demonstrated by sparking the gas over mercury when calomel, Hg_2Cl_2, and hydrogen are produced ; also by heating the gas to a high temperature in a porcelain jacket containing a central water-cooled tube of amalgamated copper, which becomes coated with chlorides of mercury and copper.

Combination of Chlorine with other Non-metals.

Chlorine combines directly with many non-metals, but has no direct action upon oxygen, nitrogen, or carbon, the chlorides of which are prepared indirectly, *e.g.*, by substitution of chlorine for hydrogen or sulphur in their compounds with these elements, thus,

$$NH_3 + 3Cl_2 = NCl_3 + 3HCl.$$
$$CS_2 + 2Cl_2 = CCl_4 + S_2.$$

(*a*) *Sulphur and Phosphorus.*—Chlorine combines directly with sulphur to form the compounds S_2Cl_2 and SCl_4. Phosphorus ignites spontaneously in chlorine, forming a liquid trichloride, PCl_3, and a solid pentachloride, PCl_5.

(*b*) *Carbon, Silicon, and Boron.*—Chlorine does not combine directly with carbon. as is shown by the fact that it is a most effective agent for

removing the last traces of hydrogen from charcoal (p. 80). It combines directly, however, with silicon to form silicon tetrachloride, $SiCl_4$, and with boron to form boron trichloride, BCl_3.

(c) *Bromine and Iodine.*—Liquid chlorine and bromine will mix in all proportions, but on cooling only isomorphous mixtures of these

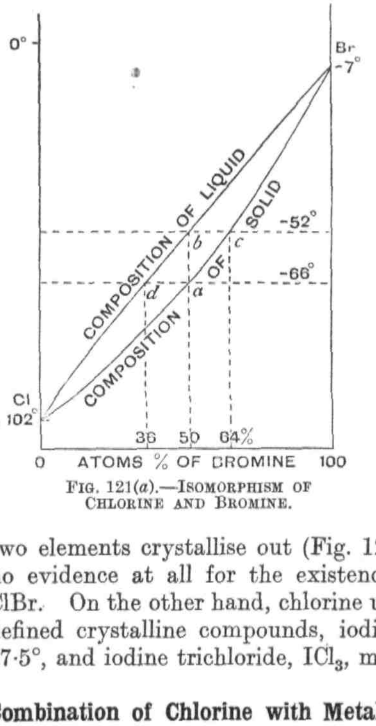


FIG. 121(*a*).—ISOMORPHISM OF CHLORINE AND BROMINE.

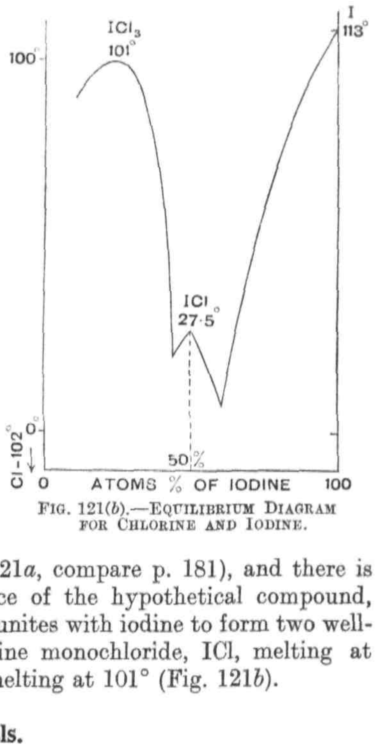


FIG. 121(*b*).—EQUILIBRIUM DIAGRAM FOR CHLORINE AND IODINE.

two elements crystallise out (Fig. 121*a*, compare p. 181), and there is no evidence at all for the existence of the hypothetical compound, ClBr. On the other hand, chlorine unites with iodine to form two well-defined crystalline compounds, iodine monochloride, ICl, melting at 27·5°, and iodine trichloride, ICl_3, melting at 101° (Fig. 121*b*).

Combination of Chlorine with Metals.

Chlorine unites directly with practically all the metals to form metallic chlorides, *e.g.*,

Zinc chloride,	Zn	+	Cl_2	=	$ZnCl_2$
Ferric chloride,	2Fe	+	$3Cl_2$	=	$2FeCl_3$
Stannic chloride,	Sn	+	$2Cl_2$	=	$SnCl_4$
Silver chloride,	2Ag	+	Cl_2	=	2AgCl
Auric chloride,	2Au	+	$3Cl_2$	=	$2AuCl_3$.

The action will usually take place in the cold, but is easily stopped by the formation of a protecting layer of chloride; this may be got rid of by vaporisation, as in the case of ferric chloride, or by fusion, as in the case of silver chloride. Some finely-divided metals take fire and burn in chlorine; this is shown most readily in the case of metallic antimony

or of "Dutch leaf," a malleable alloy of copper and zinc which can be beaten out into very thin foil.

Addition of Chlorine to Unsaturated Compounds.

Chlorine also combines directly with a large number of unsaturated compounds in which the combining power of the constituent elements is not yet fully satisfied, *e.g.*,

(*a*) With carbon monoxide and sulphur dioxide, in sunlight or in presence of a catalyst, to form carbonyl chloride (p. 462), and sulphuryl chloride (p. 333).

$$CO + Cl_2 = \underset{\text{Carbonyl chloride}}{COCl_2}.$$

$$SO_2 + Cl_2 = \underset{\text{Sulphuryl chloride}}{SO_2Cl_2}.$$

(*b*) With unsaturated hydrocarbons such as ethylene and acetylene :

$$C_2H_4 + Cl_2 = \underset{\text{Ethylene dichloride}}{C_2H_4Cl_2}.$$

$$C_2H_2 + 2Cl_2 = \underset{\text{Acetylene tetrachloride}}{C_2H_2Cl_4}.$$

(*c*) With lower chlorides of the metals and non-metals:

$$\underset{\text{Ferrous chloride}}{2FeCl_2} + Cl_2 = \underset{\text{Ferric chloride}}{2FeCl_3}. \quad S_2Cl_2 + 3Cl_2 = 2SCl_4.$$

$$\underset{\text{Stannous chloride}}{SnCl_2} + Cl_2 = \underset{\text{Stannic chloride}}{SnCl_4}. \quad PCl_3 + Cl_2 = PCl_5.$$

Displacement of Hydrogen by Chlorine.

Chlorine acts upon many hydrides, and especially upon the saturated hydrocarbons, by substitution, one atom of hydrogen being displaced by each atom of chlorine that enters the molecule. Thus, when equal volumes of marsh gas or methane, CH_4, and chlorine are exposed to sunlight, methyl chloride, CH_3Cl, is formed as the first of a series of substitution-products of which the final member is carbon tetrachloride, CCl_4.

$$CH_4 + Cl_2 = HCl + CH_3Cl \text{ (methyl chloride)}.$$
$$CH_3Cl + Cl_2 = HCl + CH_2Cl_2 \text{ (methylene chloride)}.$$
$$CH_2Cl_2 + Cl_2 = HCl + CHCl_3 \text{ (chloroform)}.$$
$$CHCl_3 + Cl_2 = HCl + CCl_4 \text{ (carbon tetrachloride)}.$$

The final product is a compound of chlorine with carbon only, which cannot be prepared by direct combination of these elements.

In the same way, the action of an excess of chlorine on ammonia leads to the displacement of the whole of the hydrogen by chlorine, the

product being a highly explosive nitrogen trichloride, which cannot be prepared by direct combination:

$$NH_3 + 3Cl_2 = 3HCl + \underset{\text{Nitrogen trichloride}}{NCl_3}.$$

Displacement of Oxygen by Chlorine.

(*a*) *Chlorination of Oxides.*—In some cases chlorine will displace oxygen directly from its compounds, as, for instance, when oxygen is set free by heating quicklime to redness in a stream of chlorine (Davy) or in the vapour of mercuric chloride:

$$2CaO + 2Cl_2 = 2CaCl_2 + O_2.$$
$$2CaO + 2HgCl_2 = 2CaCl_2 + O_2 + 2Hg.$$

More usually this action is effected with the assistance of an element, such as carbon or phosphorus, which has a great affinity for oxygen, *e.g.*, aluminium oxide may be converted into aluminium chloride and a part of the oxygen in sulphur dioxide and in sulphur trioxide may be replaced by chlorine by using the agents shown in the following equations:

$$Al_2O_3 + 3C + 3Cl_2 = \underset{\text{Aluminium chloride}}{2AlCl_3} + 3CO.$$

$$SO_2 + PCl_5 = \underset{\text{Thionyl chloride}}{SOCl_2} + POCl_3.$$

$$2SO_3 + CCl_4 = \underset{\text{Pyrosulphuryl chloride}}{S_2O_5Cl_2} + COCl_2.$$

In a similar manner, ferric oxide can be eliminated from sand, for use in the manufacture of glass, by heating in a current of carbonyl chloride,

$$Fe_2O_3 + 3COCl_2 = 2FeCl_3 + 3CO_2.$$

(*b*) *Decomposition of Chlorine-water.*—The oxidation of gaseous hydrogen chloride by gaseous oxygen in presence of cupric chloride as a catalyst has been described above as the basis of the Deacon process for manufacturing chlorine. The conditions are, however, modified profoundly when water is present, on account of the very large amount of heat that is liberated when hydrogen chloride is dissolved in water. The relevant data are as follows:

Hydrogen chloride	Heat of formation, HCl (gas)	= + 22,000 cal.
	Heat of solution	= + 17,400 cal.
	Heat of formation, HCl, aq.	= + 39,400 cal.
Water	Heat of formation, H_2O (liq.)	= + 68,360 cal.
	Latent heat (say)	+ 10,360 cal.
	Heat of formation, H_2O (gas)	= + 58,000 cal.
Chlorine	Heat of solution, Cl_2, aq.	= + 4,870

These data may be combined into equations showing the heats of oxidation of hydrogen chloride as a gas and in solution as follows :—

$$\underset{2 \times 22{,}000\ \text{cal.}}{2HCl\ (gas)} + \tfrac{1}{2}O_2\ (gas) \rightleftharpoons \underset{58{,}000\ \text{cal.}}{H_2O\ (gas)} + Cl_2\ (gas) + 14{,}000\ \text{cal.}$$

$$\underset{2 \times 39{,}400\ \text{cal.}}{2HCl,\ aq.} + \tfrac{1}{2}O_2\ (gas) \rightleftharpoons \underset{68{,}360\ \text{cal.}}{H_2O\ (liq.)} + \underset{4{,}870\ \text{cal.}}{Cl_2,\ aq.} - 5{,}570\ \text{cal.}$$

It will be seen that the oxidation of hydrogen chloride, although strongly exothermic in the gaseous state, becomes endothermic in the solution in water.

In order to bring about these changes at atmospheric temperatures, it is necessary to make use of the catalytic power of light. Thus, when a half-filled bottle of hydrochloric acid is exposed to light, *e.g.*, during a summer vacation, it smells strongly of chlorine as a result of an endothermic oxidation in which the light acts both as catalyst and as a source of energy. The converse action which results in an exothermic conversion of chlorine-water into hydrochloric acid and oxygen takes place with actual effervescence of oxygen when chlorine-water is exposed to bright tropical sunlight. The action is, however, practically stopped when chlorine is exposed, even to bright tropical sunlight, in contact with only a small quantity of water instead of the large excess which is required to dissolve the gas ; this may perhaps be explained by the strongly endothermic character of the action when carried out with gaseous chlorine and only an equivalent quantity of liquid water, thus

$$\underset{68{,}360\ \text{cal.}}{H_2O\ (liq.)} + Cl_2\ (gas) \rightleftharpoons \underset{2 \times 22{,}000\ \text{cal.}}{2HCl\ (gas)} + \tfrac{1}{2}O_2\ (gas) - 24{,}360\ \text{cal.}$$

(*c*) *Other Products of Decomposition of Chlorine-water.*—In the dark, or in diffused daylight, chlorine-water appears to decompose reversibly, with formation of hydrochloric and hypochlorous acids, as shown in the equation

$$Cl_2 + H_2O \rightleftharpoons HCl + \underset{\text{Hypochlorous acid}}{HClO}.$$

This action may be compared with the non-reversible action of chlorine on cold alkalies, *e.g.*,

$$Cl_2 + 2KOH = KCl + KClO + H_2O,$$

and has been advanced as an explanation of the electrical conductivity of chlorine-water. The hypochlorous acid formed in this way may then decompose with liberation of oxygen,

$$2HClO = 2HCl + O_2,$$

or may change into hydrochloric and chloric acids,

$$3HClO = 2HCl + \underset{\text{Chloric acid}}{HClO_3},$$

compare

$$3KClO = 2KCl + KClO_3.$$

The former action predominates in bright tropical sunlight, when chlorine-water gives almost a quantitative yield of oxygen (1 *vol.* of Cl_2 gives $\frac{1}{2}$ *vol.* of O_2), but in diffused sunlight chloric acid is formed and the yield of oxygen is much less.

(*d*) *Oxidation by Chlorine.*—The liberation of oxygen from water by chlorine affords a convenient method of bringing about oxidation in aqueous solutions. On account of this property, chlorine-water is an important oxidising agent.

(i) Direct oxidation by means of chlorine-water occurs in the following cases:

$$\underset{\text{Sulphurous acid}}{H_2SO_3} + H_2O + Cl_2 = \underset{\text{Sulphuric acid}}{H_2SO_4} + 2HCl.$$

$$\underset{\text{Potassium sulphide}}{K_2S} + 4H_2O + 4Cl_2 = \underset{\text{Potassium sulphate}}{K_2SO_4} + 8HCl.$$

(ii) The removal of hydrogen or of a metal by chlorine is also classed as an "oxidation," although there is no actual transference of oxygen, and water does not appear in the equations:

$$H_2S + Cl_2 = 2HCl + S.$$

$$2HI + Cl_2 = 2HCl + I_2.$$

$$\underset{\text{Potassium manganate}}{2K_2MnO_4} + Cl_2 = 2KCl + \underset{\text{Potassium permanganate}}{2KMnO_4}.$$

(iii) In the same way, the mere addition of chlorine to convert a ferrous salt into a ferric salt, or a stannous salt into a stannic salt, is regarded as an "oxidation," in view of the fact that the products are derived from higher oxides of the metals:

$$\underset{\text{Ferrous chloride}}{2FeCl_2} + Cl_2 = \underset{\text{Ferric chloride}}{2FeCl_3}, \text{ compare } \underset{\text{Ferrous oxide}}{4FeO} + O_2 = \underset{\text{Ferric oxide}}{2Fe_2O_3}.$$

$$\underset{\text{Stannous chloride}}{SnCl_2} + Cl_2 = \underset{\text{Stannic chloride}}{SnCl_4}, \text{ compare } \underset{\text{Stannous oxide}}{2SnO} + O_2 = \underset{\text{Stannic oxide}}{2SnO_2}.$$

In these cases also chlorine can be used instead of chlorine-water as the "oxidising agent."

(iv) Bleaching by means of chlorine is also an oxidising action; but in view of the special efficiency of hypochlorous acid as a bleaching agent it is possible that this is the active material even in chlorine-water, which is known to yield hypochlorous acid according to the equation

$$Cl_2 + H_2O \rightleftharpoons HCl + HClO.$$

Displacement of Sulphur by Chlorine.

(*a*) *Metallic Sulphides.*—Chlorine acts readily upon metallic sulphides, converting them into chlorides and liberating sulphur. This

action was observed by Scheele in the case of cinnabar or mercuric sulphide, HgS, which is converted by the action of chlorine into corrosive sublimate or mercuric chloride, $HgCl_2$:

$$HgS + Cl_2 = HgCl_2 + S.$$

A similar action occurs when the mixed sulphide ores of the Broken Hill district of Australia, which contain blende (zinc sulphide), galena (lead sulphide), and silver glance (silver sulphide), are acted upon by chlorine:

$$ZnS + Cl_2 = ZnCl_2 + S.$$
$$PbS + Cl_2 = PbCl_2 + S.$$
$$Ag_2S + Cl_2 = 2AgCl + S.$$

The product is a liquid mixture of zinc, lead, and silver chlorides, from which the silver can be recovered by the action of lead

$$2AgCl + Pb = PbCl_2 + 2Ag;$$

the lead can then be precipitated by means of zinc,

$$PbCl_2 + Zn = ZnCl_2 + Pb;$$

and finally the zinc and the whole of the chlorine can be recovered by electrolysis,

$$ZnCl_2 = Zn + Cl_2.$$

During this cycle of operations there is no marked loss of chlorine, since the whole of the sulphur is liberated in the free state and not in the form of chlorides; but the process is complicated by the presence of iron and manganese, which must be removed by a wet method before the zinc chloride is electrolysed.

(*b*) *Sulphides of Non-metals.*—Displacement of sulphur by chlorine is also observed in sulphuretted hydrogen, from which sulphur is precipitated by chlorine,

$$H_2S + Cl_2 = 2HCl + S,$$

and in carbon disulphide, which can be converted into carbon tetrachloride by the action of chlorine, or more conveniently of sulphur chloride:

$$CS_2 + 2Cl_2 = CCl_4 + S_2$$
$$2CS_2 + 2SCl_4 = 2CCl_4 + 3S_2.$$

CHLORINE and HYDROGEN.

Preparation of Hydrogen Chloride.

Hydrogen chloride is prepared by the action of sulphuric acid on common salt. The action proceeds in two stages, sodium hydrogen sulphate being formed first, and neutral sodium sulphate only when the temperature is raised,

$$NaCl + H_2SO_4 = HCl + NaHSO_4$$
$$NaCl + NaHSO_4 = HCl + Na_2SO_4.$$

This process was formerly carried out on a large scale as part of the Le Blanc process for manufacturing soda (p. 569).

The chief impurities in commercial hydrochloric acid are sulphuric acid, ferric chloride, arsenic, and either sulphur dioxide or chlorine. In order to purify it, the acid is diluted to 25% HCl and strips of copper are immersed in it; arsenic and free chlorine are thus removed in combination with copper, whilst ferric chloride is reduced to ferrous chloride and remains behind during the subsequent distillation.

Hydrogen chloride can be prepared on a small scale from rock salt and oil of vitriol by means of the apparatus shown in Fig. 122. Oil of vitriol is slowly dropped from a funnel, *F*, on to rock salt contained in a large flask, *E*. The flow of acid is regulated by a tap, and any excess of hydrogen chloride is allowed to escape by a side tube, *B*, where it passes through a mercury trap, *C*, and is absorbed by water at *D*. The action begins at atmospheric temperatures, but towards the end it is necessary to warm the flask in order to maintain the flow of gas. The gas may be collected over mercury or by displacement of air. A regular supply of the gas may also be obtained, without external heat, by dropping strong sulphuric acid into commercial muriatic acid.

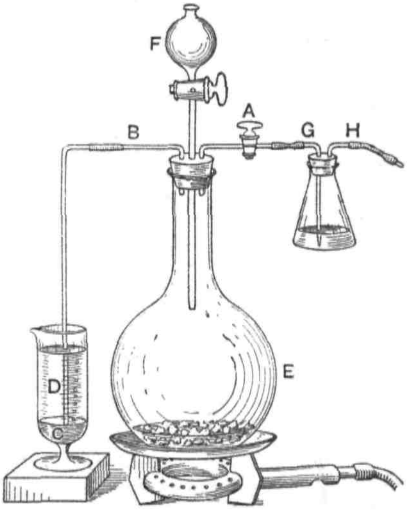


FIG. 122.—APPARATUS FOR PREPARATION OF HYDROGEN CHLORIDE.

The apparatus as shown in Fig. 122 is arranged for the preparation of a standard solution of hydrogen chloride by Moody's method. A small conical flask is provided with a rubber stopper carrying two tubes, *G* and *H*. The tube *G* passes down to a capillary at the bottom of the flask, whilst the tube *H* carries a rubber tube which can be closed with a glass plug. When all the air has been driven out from the large flask, *E*, the small conical flask, previously weighed with its fittings and a suitable quantity of water, is attached to the tap-tube, *A*; before opening the tap, air is sucked out through the tube *H* to create a partial vacuum and this tube is closed with a glass rod. By opening the tap *A*, hydrogen chloride is admitted to the small flask, where it is absorbed completely by the water. When a sufficient quantity of the gas has been absorbed, as judged by the rising temperature of the water, the flask is detached at *G*, the gas in *G* being drawn into the flask by the partial vacuum; the flask is closed at *G* with a rubber tube and glass rod, allowed to cool, and weighed. The increase in the weight of the flask gives the weight of hydrogen chloride absorbed, and this can be washed out and diluted to a known volume of standard solution.

Physical Properties of Hydrogen Chloride.

Hydrogen chloride is a colourless gas, with a pungent suffocating odour, which fumes strongly in most air. It is not inflammable and does not support combustion, but at high temperatures it begins to dissociate into its elements, the dissociation reaching 0·27 per cent. at 1537° (see Table 35, p. 276). The critical temperature of the gas is 52° and the critical pressure 83 atmospheres; at atmospheric temperatures it can be condensed, under a vapour pressure of about 50 atmospheres (at 26°), to a colourless liquid, which does not conduct electricity and is chemically inactive. The liquid boils at − 83° under atmospheric pressure, when its density is 1·185, and on further cooling forms a crystalline solid melting at − 111°.

Hydrogen Chloride and Water.

Hydrogen chloride is extremely soluble in water, which dissolves 500 volumes of the gas (as compared with 1300 volumes of ammonia) at 0°, and 440 volumes at 20°. A solution saturated at 18° contains 42 per cent. of the gas. The solubility diminishes with rising temperature, gas being driven off from the saturated solution until at 110° an acid containing 20·24 per cent. of HCl distils over as a mixture of constant boiling-point. Conversely, dilute hydrochloric acid loses water when distilled; the acid remaining behind therefore becomes more and more concentrated, and its boiling-point rises continually, until an acid containing 20·24 per cent. of HCl again distils at a constant boiling-point of 110° (compare p. 177).

It was thought at one time that this HYDROCHLORIC ACID OF MAXIMUM BOILING-POINT was a chemical compound which could be represented by a definite formula, *e.g.*, $HCl,8H_2O$ would contain 20·24 per cent. of hydrogen chloride; but Roscoe and Dittmar showed that the acid varies in composition with the pressure, *e.g.*, from 18 per cent. of hydrogen chloride at 2500 mm. to 23·2 per cent. at 50 mm., and cannot therefore be a pure compound. It is, however, possible that the mixture is a compound of hydrogen chloride and water mixed with the products of dissociation,

$$HCl,nH_2O \rightleftharpoons HCl + nH_2O,$$

in proportions varying with the pressure under which distillation is carried out.

Three definite hydrates can be frozen out from aqueous solutions of hydrogen chloride, namely,

Hydrate.	*Melting-point.*
HCl,H_2O	− 15·35°
$HCl,2H_2O$	− 17·7°
$HCl,3H_2O$	− 24·9°

These compounds evidently dissociate when melted, but the presence

of hydrates in the liquid is proved clearly by the large amount of heat that is liberated when hydrogen chloride dissolves in water,

$$HCl + Aq = HCl, aq + 17{,}500 \text{ calories.}$$

This evolution of heat is not due entirely to the latent heat of liquefaction of the hydrogen chloride, which amounts only to 3,600 calories, or 20 per cent. of the total; the remaining 80 per cent. must be attributed to chemical combination between hydrogen chloride and water. The existence of hydrates, even at the boiling-point of the acid, must also be assumed in order to account for the fact that the addition of a gas boiling at − 83° is able to raise the boiling-point of water from 100° to 110°.

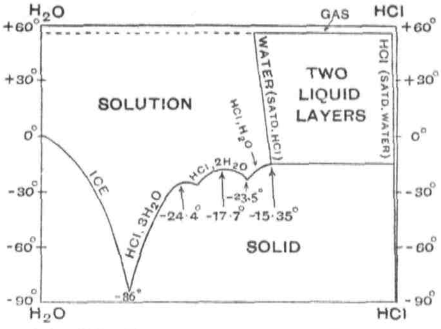


FIG. 123.—EQUILIBRIUM BETWEEN HYDROGEN CHLORIDE AND WATER.

The conditions of equilibrium between hydrogen chloride and water are shown in Fig. 123.

Chemical Properties of Hydrogen Chloride.

(*a*) *Action on Metals.*—Hydrogen chloride, liquefied by pressure or by cooling, does not act on metals (except aluminium) and appears to possess no acid qualities. When mixed with water it forms a very strong acid, although its strength is somewhat disguised by the readiness with which it can be vaporised. Thus, oil of vitriol acting on solid rock salt, or even upon concentrated aqueous hydrochloric acid, drives out gaseous hydrogen chloride; but when vaporisation is prevented hydrochloric acid is approximately twice as strong as sulphuric acid, *e.g.*, in competition for a quantity of caustic soda insufficient to neutralise both.

Hydrochloric acid dissolves most of the base metals with evolution of hydrogen, *e.g.*,

$$Zn + 2HCl = ZnCl_2 + H_2;$$
$$Fe + 2HCl = FeCl_2 + H_2;$$
$$Sn + 2HCl = SnCl_2 + H_2;$$

in the case of iron and tin, ferrous chloride, $FeCl_2$, and stannous chloride, $SnCl_2$, are formed, where free chlorine gives ferric chloride, $FeCl_3$, and stannic chloride, $SnCl_4$. Copper dissolves slowly on boiling with concentrated hydrochloric acid, forming cuprous chloride and hydrogen,

$$2Cu + 2HCl = Cu_2Cl_2 + H_2;$$

in this action the energy of combination of cupric chloride with copper,

$$Cu + CuCl_2 = Cu_2Cl_2,$$

is apparently sufficient to turn the scale in favour of the dissolution of a metal which is not usually attacked except by acids which are also oxidising agents. Silver dissolves slowly in concentrated hydrochloric acid in presence of air,

$$4Ag + 4HCl + O_2 = 4AgCl + 2H_2O,$$

the chloride, which is insoluble in water, dissolving readily in the strong acid. The precious metals, platinum and gold, do not dissolve in hydrochloric acid, but AQUA REGIA dissolves them readily, probably as a result of the liberation of chlorine from the acid mixture, *e.g.*,

$$3HCl + HNO_3 = Cl_2 + NOCl + 2H_2O.$$

When gold is present, the action is represented by the equation

$$Au + 4HCl + HNO_3 = HAuCl_4 + NO + 2H_2O.$$

(*b*) *Action on Bases.*—Hydrogen chloride combines directly with *ammonia*, in presence of traces of moisture, to form ammonium chloride,

$$NH_3 + HCl = NH_4Cl.$$

It also forms salts with metallic *oxides*, water being eliminated in the process:

$$PbO + 2HCl = PbCl_2 + H_2O.$$

With *carbonates*, water and carbon dioxide are set free,

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2.$$
$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

Chlorine and Oxygen.

Oxides and Oxy-acids of Chlorine.

Chlorine does not unite directly with oxygen, but three oxides can be prepared by indirect methods, namely,

Dichlorine monoxide, Cl_2O,
Chlorine dioxide, ClO_2, and
Dichlorine heptoxide, Cl_2O_7.

A full series of oxy-acids is also known, either in the free state or in the form of salts. In accordance with the general system of nomenclature, the commonest of these acids, $HClO_3$, is selected as the typical oxy-acid, and is described as CHLORIC ACID, whilst its salts are called CHLORATES. An acid, $HClO_4$, richer in oxygen is called PERCHLORIC ACID and its salts are called PERCHLORATES. An acid, $HClO_2$, containing less oxygen is called CHLOROUS ACID, and its salts are called CHLORITES; and finally an acid, HClO, containing still less oxygen is called HYPOCHLOROUS ACID and its salts are called HYPOCHLORITES.

The whole series of oxides, acids, and sodium salts is set out, with HYDROCHLORIC ACID and the CHLORIDES, in the following list :—

Oxide.	*Acid.*	*Sodium salt.*
	Hydrochloric acid, HCl	Sodium chloride, $NaCl$
Dichlorine monoxide, Cl_2O	Hypochlorous acid, $HClO$	Sodium hypochlorite, $NaClO$
Chlorine dioxide, ClO_2	Chlorous acid, $HClO_2$	Sodium chlorite, $NaClO_2$
	Chloric acid, $HClO_3$	Sodium chlorate, $NaClO_3$
Dichlorine heptoxide, Cl_2O_7	Perchloric acid, $HClO_4$	Sodium perchlorate, $NaClO_4$

Action of Chlorine on the Alkalies.

It has been suggested (p. 280) that chlorine-water may owe its electrical conductivity to a balanced action which results in the formation of traces of hydrochloric and hypochlorous acids,

$$Cl_2 + H_2O \rightleftharpoons HCl + HClO,$$

and that in diffused daylight some of the hypochlorous acid may be decomposed into hydrochloric and chloric acids,

$$3HClO = 2HCl + HClO_3.$$

Similar changes occur when alkalies are present, but these neutralise the acid products and bring about a complete conversion into salts of the above acids. Thus, the action of chlorine on a cold solution of potassium hydroxide yields potassium chloride and **potassium hypochlorite**, $KClO$, as shown in the equation

$$2KOH + Cl_2 = KCl + KClO + H_2O;$$

whilst in a hot solution, potassium chloride and **potassium chlorate**, $KClO_3$, are formed according to the equation

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

Potassium chlorite, $KClO_2$, is produced, with potassium chlorate, by the action of chlorine dioxide on caustic potash,

$$2KOH + 2ClO_2 = KClO_2 + KClO_3 + H_2O$$

whilst **sodium chlorite**, $NaClO_2$, can be produced by the interaction of chlorine dioxide with sodium peroxide,

$$Na_2O_2 + 2ClO_2 = 2NaClO_2 + O_2$$

Potassium perchlorate, $KClO_4$, is formed from the chlorate by gentle heating,

$$4KClO_3 = 3KClO_4 + KCl,$$

or by electrolytic oxidation,

$$KClO_3 + O = KClO_4.$$

From these salts, which are described more fully in Chapter XXXII, the oxides and oxy-acids of chlorine are commonly prepared, but it is noteworthy that only the acids containing the highest proportions of oxygen are sufficiently stable to be isolated readily.

Oxy-acids of Chlorine.

Hypochlorous acid, HClO, is formed when dichlorine monoxide is dissolved in water,

$$Cl_2O + H_2O = 2HClO,$$

and (with hydrochloric acid) by the action of chlorine on water,

$$Cl_2 + H_2O \rightleftharpoons HCl + HClO.$$

Small quantities can be prepared by the action of chlorine on freshly-precipitated yellow mercuric oxide suspended in water,

$$2HgO + 2Cl_2 + H_2O = HgO{,}HgCl_2 + 2HClO,$$

the insoluble basic mercuric chloride being removed by filtration. This action is analogous with that of chlorine on caustic potash, but differs from it in that the mercuric oxide is too weak a base to hold the weak hypochlorous acid, which is therefore obtained as a free acid.

Hypochlorous acid is prepared on a large scale by the action of carbon dioxide on bleaching powder suspended in ice-cold water,

$$2CaOCl_2 + CO_2 + H_2O = CaCO_3 + CaCl_2 + 2HClO.$$

The characteristic odour of bleaching powder, which is quite distinct from that of chlorine, is probably due to hypochlorous acid liberated in this way by atmospheric carbon dioxide.

Hypochlorous acid is very volatile and its odour can easily be detected. Solutions of hypochlorous acid in water are golden-yellow in colour and very unstable. When exposed to light they decompose according to the equations

$$2HClO = 2HCl + O_2$$
$$3HClO = 2HCl + HClO_3;$$

when mixed with hydrochloric acid, chlorine is set free according to the equation

$$HClO + HCl \rightleftharpoons Cl_2 + H_2O.$$

A solution of hypochlorous acid may be distinguished from chlorine-water by shaking with mercury, when hypochlorous acid produces a brownish-yellow precipitate of basic mercuric chloride, whilst chlorine-water produces a white precipitate of calomel,

$$Hg + HClO = Hg(OH)Cl$$
$$2Hg + Cl_2 = Hg_2Cl_2.$$

Hypochlorous acid is a powerful oxidising and bleaching agent

and is perhaps the active agent in bleaching by means of hypochlorites or of bleaching powder. In the latter case, the fabric to be bleached is boiled with dilute sodium hydroxide, immersed in a very dilute solution of bleaching powder, and left exposed to the air for several hours, when bleaching is effected probably through the agency of atmospheric carbon dioxide liberating hypochlorous acid as shown above. The fabric is then placed in a bath of very dilute sulphuric acid, in order to destroy any traces of bleaching powder which still remain, and may also be freed from the last traces of chlorine by the action of sulphurous acid or a sulphite (p. 331).

Chlorous acid, $HClO_2$, was prepared recently (in 1912) by adding sulphuric acid to a solution of barium chlorite and filtering off the precipitated barium sulphate,

$$Ba(ClO_2)_2 + H_2SO_4 = BaSO_4 + 2HClO_2.$$

The solution is colourless, and decomposes at atmospheric temperatures into hypochlorous and chloric acids

$$2HClO_2 = HClO + HClO_3.$$

Chloric acid, $HClO_3$, cannot be prepared by the action of strong sulphuric acid on potassium chlorate, but is formed when an aqueous solution of barium chlorate is precipitated with sulphuric acid,

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3.$$

After filtering off the barium sulphate, the solution can be concentrated over sulphuric acid in a vacuum until it contains 40 per cent. of the acid. On further concentration, or on heating the solution, the acid is decomposed, perchloric acid being formed and chlorine dioxide set free,

$$3HClO_3 = HClO_4 + 2ClO_2 + H_2O.$$

Chloric acid is a powerful oxidising agent, and wood is ignited by the strong solution. The acid oxidises sulphuretted hydrogen to sulphur and water, and sulphur dioxide to sulphuric acid,

$$2HClO_3 + 4H_2S = 4S + 5H_2O + Cl_2O$$
$$2HClO_3 + 3H_2O + 4SO_2 = 4H_2SO_4 + Cl_2O.$$

The last reaction affords a test for chloric acid ; this acid does not oxidise indigo directly, but when sulphur dioxide is added, indigo is decolorised by the dichlorine monoxide shown as a product of reduction of chloric acid in the preceding equations.

Perchloric acid, $HClO_4$, the most stable acid of this series, resembles sulphuric anhydride in many of its properties, whilst its monohydrate possesses some analogies with sulphuric acid. It can be prepared by distilling under reduced pressure a mixture of potassium perchlorate and strong sulphuric acid :

$$KClO_4 + H_2SO_4 = KHSO_4 + HClO_4.$$

Perchloric acid melts at $-112°$ and boils at 16° under a pressure of 18 mm. It unites violently with water, forming a series of hydrates.

TABLE 36.—HYDRATES OF PERCHLORIC ACID.

Hydrate.	*Melting-point.*
$HClO_4,H_2O$	$+ 50°$
$HClO_4,2H_2O$	$- 18°$
$HClO_4,2{\cdot}5H_2O$	$- 30°$
$HClO_4,3H_2O$	$- 37°$
$HClO_4,3{\cdot}5H_2O$	$- 41°$

A mixture of constant boiling-point containing 71·6 per cent. of perchloric acid distils at 203° as an oily liquid resembling sulphuric acid.

Perchloric acid is a powerful oxidising agent, which inflames paper and wood, produces burns on the skin, and is liable to decompose violently. As in the case of sulphur trioxide, however, its oxidising properties disappear in dilute solutions, which are not reduced by sulphur dioxide.

Oxides of Chlorine.

Dichlorine monoxide, Cl_2O, is prepared by passing chlorine over dried precipitated yellow mercuric oxide cooled to 0° by means of ice. A residue of basic mercuric chloride is left in the apparatus, in the form of brown crystals:

$$2HgO + 2Cl_2 = Cl_2O + HgO,HgCl_2.$$

Dichlorine monoxide is a brownish-yellow gas which may be condensed to a dark brown liquid, boiling at 20°. It is a strongly endothermic compound, and explodes when heated, as well as on the addition of flowers of sulphur or of organic matter.

Chlorine dioxide or **chlorine peroxide**, ClO_2, is prepared by the action of sulphuric acid on potassium chlorate:

$$3KClO_3 + 3H_2SO_4 = 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O.$$

A mixture of chlorine dioxide with carbon dioxide is produced by heating dilute sulphuric acid, potassium chlorate, and oxalic acid to a temperature of 70°:

$$2KClO_3 + H_2C_2O_4 + H_2SO_4 = K_2SO_4 + 2ClO_2 + 2CO_2 + 2H_2O.$$

When potassium chlorate is heated with hydrochloric acid a mixture of chlorine and chlorine dioxide is produced, which Davy described as a definite compound under the name of EUCHLORINE:

$$8KClO_3 + 24HCl = 8KCl + 12H_2O + 9Cl_2 + 6ClO_2.$$

Chlorine dioxide is a brownish-yellow gas with a peculiar smell. It condenses to a reddish-brown liquid boiling at 9·9° under a pressure of 731 mm. and forms orange crystals melting at $-76°$.

Chlorine dioxide dissolves in water to form a mixture of chloric and chlorous acids, which possesses bleaching properties:

$$2ClO_2 + H_2O = HClO_3 + HClO_2.$$

It also interacts with sodium peroxide, forming sodium chlorite:

$$2ClO_2 + Na_2O_2 = 2NaClO_2 + O_2.$$

The gas and liquid explode violently when heated or in the presence of organic matter. This explains the "crackling" produced when strong sulphuric acid acts on potassium chlorate, an action which distinguishes the chlorates from the more stable perchlorates. Phosphorus catches fire when dropped into a jar of chlorine dioxide.

Dichlorine heptoxide or **perchloric anhydride**, Cl_2O_7, the most stable of the oxides of chlorine, is obtained by adding perchloric acid slowly to phosphoric oxide cooled below $-10°$.

$$P_2O_5 + 6HClO_4 = 2H_3PO_4 + 3Cl_2O_7.$$

The mixture is kept at $-10°$ for a day and is then slowly warmed on a water-bath until the dichlorine heptoxide distils over.

It is a colourless oil, boiling at 82°, which explodes violently on percussion, but is without action on wood or paper. It dissolves in water and is converted slowly into perchloric acid:

$$Cl_2O_7 + H_2O = 2HClO_4.$$

Detection of Chlorine.

Chlorine in the uncombined state may be detected by its smell and by its action in liberating iodine from potassium iodide*; the iodide is mixed with starch solution, which is coloured blue by the iodine. Aniline hydrochloride is coloured red by free chlorine, and the colour changes to blue on exposure to the air.

A solution of an inorganic chloride yields a white precipitate of silver chloride, AgCl (which is insoluble in nitric acid, but soluble in ammonia), on the addition of an aqueous solution of silver nitrate.

Organic chlorine-compounds do not usually give a precipitate with silver nitrate, but when they are heated with strong nitric acid and silver nitrate in a sealed tube, silver chloride is formed.

A simple (but not exclusive) test for chlorine in organic compounds consists in holding a piece of copper wire in a Bunsen flame until the green colour disappears from the flame, dipping the wire in the chlorine-compound, and replacing it in the flame, which shows the green flame-colour of copper chloride if chlorine is present.

Estimation of Chlorine.

Free chlorine is estimated by adding an excess of potassium iodide and titrating the liberated iodine with an aqueous solution of sodium thiosulphate:

$$Cl_2 + 2KI = 2KCl + I_2.$$
$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6 \text{ (sodium tetrathionate).}$$

* Many other substances liberate iodine from potassium iodide, *e.g.*, bromine, oxides of nitrogen, ozone, hydrogen peroxide, sulphuric acid, nitric acid, and copper sulphate.

The quantity of chloride in a solution may be estimated by adding silver nitrate and nitric acid and weighing the precipitate of silver chloride thus produced (p. 154). It can be estimated volumetrically in neutral solutions by titrating with standard silver nitrate, using potassium chromate, K_2CrO_4, as an indicator ; or, in acid solutions by adding an excess of silver nitrate, and titrating back with ammonium sulphocyanide, using ferric alum as an indicator.

The total chlorine in any substance, whether inorganic or organic, may be estimated by the method of Carius. The substance is heated in a sealed tube, with pure nitric acid and silver nitrate crystals, and the precipitated silver chloride is collected and weighed.

Atomic Weight of Chlorine.

(*a*) Stas determined the atomic weight of chlorine as follows :—

(i) Potassium chlorate was heated and the residue of potassium chloride weighed ; the total weights in five experiments were :

Weight of $KClO_3$ = 498·6355 grams.
Weight of KCl = 303·3870 ,,
Weight of oxygen = 195·2485 ,,

Taking O = 16, we have

3O : KCl = 195·2485 : 303·3870 or 48 : 74·585.

In a second series of experiments the chlorate was converted into chloride by the action of hydrochloric acid ; the total weights in three experiments were as follows :

Weight of $KClO_3$ = 302·8425 grams
Weight of KCl = 184·2735 ,,
Weight of oxygen = 118·5690 ,,

3O : KCl = 118·5690 : 184·2735 or 48 : 74·592.

The mean molecular weight of KCl is therefore **74·592.**

(ii) The weight of silver required to combine with all the chlorine in potassium chloride, according to the equation

$$\underset{\text{Solution}}{KCl} + \underset{\text{Solution}}{AgNO_3} = \underset{\text{Solution}}{KNO_3} + \underset{\text{Precipitate}}{AgCl}$$

was next determined ; in twenty-three experiments,

KCl : Ag = 145·70775 : 210·85488 or 74·592 : 107·943.

∴ the atomic weight of silver = **107·943.**

(iii) Pure silver was then converted into silver chloride, in various ways ; in seven experiments the total weights were :

Weight of AgCl = 1287·7420 grams.
Weight of Ag = 969·3549 ,,

weight of chlorine = 318·3871 grams.
Ag : Cl = 969·3549 : 318·3871 or 107·943 : 35·454.
the atomic weight of chlorine = **35·454.**
the atomic weight of potassium = 74·592 − 35·454 = **39·138.**

(*b*) Dixon and Edgar burnt pure hydrogen at a fine jet in a globe containing a known weight of pure chlorine. The hydrogen was obtained by heating "palladium-hydrogen," the loss of weight of which gave the weight of hydrogen burnt. In the earlier experiments the hydrogen chloride was absorbed by water in the combustion vessel, and the unburnt chlorine, amounting to 2 per cent., was determined by adding potassium iodide, and titrating the liberated iodine. In the later experiments the hydrogen chloride was condensed in liquid air and distilled over into a second vessel for weighing. The value for the atomic weight of chlorine thus obtained was 35·462.

The apparatus used in the later experiments is shown in Fig. 124. Liquid chlorine was contained in the bulb *E* and was released (after cooling to $-25°$ with ice and calcium chloride) by breaking the glass point *H* by a

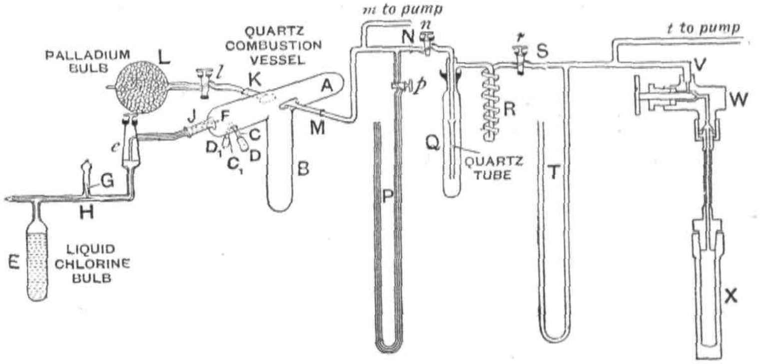


FIG. 124.—APPARATUS FOR THE COMBUSTION OF HYDROGEN AND CHLORINE. (Edgar.)

blow from a steel weight *G*, enclosed in glass to protect it from the chlorine; this weight was lifted and dropped by a magnet. The flow of chlorine to the quartz-glass combustion vessel, *A*, was controlled by a reversed tap, *e*, designed to hold tight under pressure. Hydrogen was supplied through a tap, *l*, from a palladium-bulb, *L*, which was heated to drive out the gas. The chlorine escaping from the silica jet, *F*, was ignited by sparks passing between platinum-iridium points mounted in glass in the sparking-plugs, *D*. The hydrogen chloride was condensed by liquid air in *B*, and after drawing off the uncondensed gases (unburnt hydrogen and a little nitrogen) was distilled over for weighing into the steel bomb, *X*, where it was again condensed by liquid air. During this distillation it passed through a quartz tube, *Q*, in which the unburnt chlorine was absorbed by mercury vapour, distillation of mercury into *X* being prevented by cooling the coil, *R*, to $-80°$ with solid carbon dioxide and ether. *P* and *T* are manometers, the tap *p* serving to protect the mercury in *P* from attack by chlorine during the distillation of the hydrogen chloride.

In a typical experiment the weights were as follows :

Weight of hydrogen taken	=	2·14862	grams.
,, ,, ,, unburnt	=	0·00343	,,
Weight of hydrogen burnt	=	2·14519	,,
Weight of chlorine taken	=	75·5671	,,
,, ,, ,, unburnt	=	0·0645	,,
Weight of chlorine burnt	=	75·5026	,,
Weight of hydrogen and chlorine burnt	=	77·6478	,,
Weight of hydrogen chloride caught	=	77·6469	,,
Ratio Cl : H	=	**35·196** : 1	,,
Ratio (HCl − H) : H	=	**35·196** : 1	,,

(*c*) The atomic weight of chlorine has also been determined by Guye, and by Gray and Burt, from accurate measurements of density and combining volume (p. 142).

The mean of all the recent determinations of the atomic weight of chlorine is 35·46, but the "element" is now known to be a mixture of two "isotopes" (p. 540), the atomic weights of which are 35 and 37 respectively; * the "chemical atomic weight" of 35·46 shows the proportions in which they are present in natural bodies.

* Possibly three isotopes, of 35, 37 and 39 atomic weights respectively.

CHAPTER XXIV

THE HALOGENS

9.	Fluorine,	F	=	19·0
17.	Chlorine,	Cl	=	35·46
35.	Bromine,	Br	=	79·92
53.	Iodine,	I	=	126·92

General Properties of the Halogens.

The Halogens.

Chlorine may be regarded as the typical member of a natural group of four non-metals,

fluorine, chlorine, bromine, iodine.

Fluorine has been known in the form of FLUORSPAR or **calcium fluoride**, CaF_2 (just as chlorine has been known in the form of common salt), from a very early period, since the beautiful "fluorescence" of this mineral, the characteristic intersecting cubes of which are shown in Fig. 125, could not be overlooked. The hydride, **hydrogen fluoride**, HF, has been known under the name of FLUOR ACID as an agent for etching glass since 1670, *i.e.*, from a period almost as early as that at which hydrogen chloride was first collected in water as spirit of salt. The element was, however, not isolated until 1886.

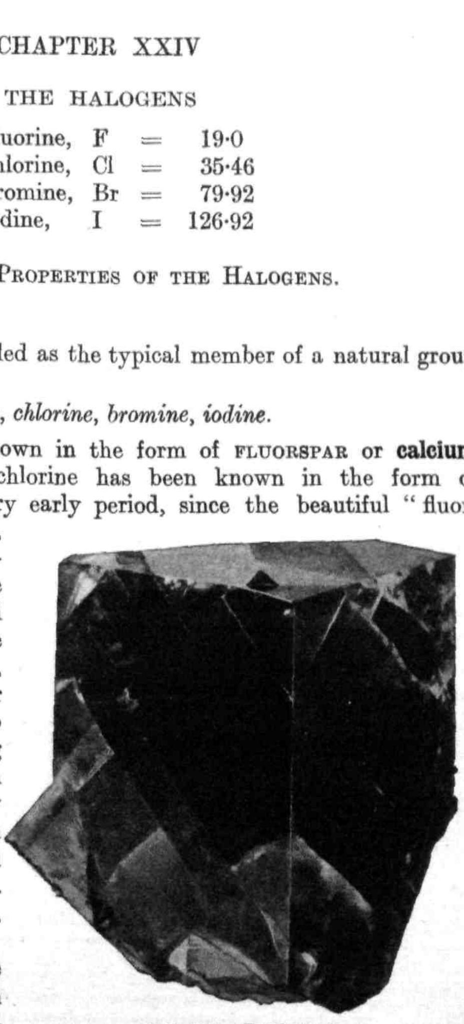


Fig. 125.—Fluorspar.

Bromine and **iodine** were only discovered in 1826 and 1812 respectively, when the elements had been liberated in a free state from saline solutions, their

compounds being unknown previously. The discovery of iodine created very great interest, not only because of the beautiful violet colour of its vapour, but also because of its close analogy to chlorine. The elementary nature of chlorine was at that time still a matter of vigorous controversy, and the discovery of iodine was a final blow to Berthollet's theory that chlorine was an oxide, since it was absurd to postulate the presence of oxygen in two substances from which it was quite impossible to extract either oxygen or any compound of oxygen.

Physical Properties of the Halogens.

The physical properties of the halogens exhibit an interesting gradation of properties which is seen in the colour, in the melting-point and boiling-point, and in the density of the solid or liquid element, as well as in properties such as vapour density, which are related more directly to the atomic weights. This gradation is shown in the following table :

TABLE 37.—PHYSICAL PROPERTIES OF THE HALOGENS.

	Atomic weight.	*Melting-point.*	*Boiling-point.*	*Density.*
Fluorine, pale yellow gas .	19·0	−233°	−187°	1·14 at −200°
Chlorine, greenish-yellow gas	35·46	−102°	− 34°	1·42 at 18°
Bromine, reddish-brown liquid	79·92	− 7°	+ 59°	3·14 at 18°
Iodine, violet solid . . .	126·92	+113°	+184°	4·94 at 17°

Chemical Properties of the Halogens.

(*a*) *Combination with Metals.*—The name HALOGEN, or "salt-producer" (p. 65), was introduced by Berzelius in 1825, in order to describe those non-metals which form salts by direct combination with metals. Binary salts produced in this way were called HALOID SALTS in order to distinguish them from AMPHI-SALTS (Greek, ἀμφί, of both kinds) formed by the union of an acid with a base.

The affinity of the halogens for metals decreases progressively from fluorine to iodine. Fluorine will therefore displace chlorine from its salts, chlorine will displace bromine, and bromine will displace iodine, *e.g.*,

$$F_2 + 2KCl = Cl_2 + 2KF$$
$$Cl_2 + 2KBr = Br_2 + 2KCl$$
$$Br_2 + 2KI = I_2 + 2KBr.$$

Even iodine, however, will unite directly with most metals, *e.g.*, two iodides of mercury can be prepared by merely rubbing the two elements together, namely, a red **mercuric iodide**, HgI_2, when iodine is in excess, and a green **mercurous iodide**, Hg_2I_2, when mercury is in excess.

(*b*) *Combination with Hydrogen.*—The four halogen elements combine

with hydrogen, but show a progressive diminution in their affinity for this element. Thus,

(i) Solid fluorine introduced into liquid hydrogen at − 253° will produce a violent explosion at a temperature at which all other chemical actions appear to be arrested.

(ii) Hydrogen and chlorine will unite with explosion only when heated or exposed to sunlight, but the product is so stable that only slight dissociation (about ¼ per cent.) occurs even at 1500°.

(iii) Bromine vapour will not explode with hydrogen, and the hydrogen bromide formed by their combination is dissociated to the same degree (about 1 per cent.) at 1200° as hydrogen chloride at 2000°.

(iv) Finally, hydrogen and iodine unite only partially at 500°, one-fourth of the material remaining uncombined. Hydrogen iodide also sets free some of its iodine on exposure to light, and parts with its hydrogen so readily as to be (like hydrogen sulphide, p. 324) an effective reducing agent.

(c) *Properties of the Hydrides.*—The physical properties and the heats of formation of the halogen-hydrides are shown in the following table:

TABLE 38.—PHYSICAL PROPERTIES OF THE HALOGEN-HYDRIDES.

	Melting-point.	*Boiling-point.*	*Heat of formation.* *Gaseous.*	*Dissolved.*
HF	− 92°	+ 19·5°	+ 38,500 cal.	+ 50,300 cal.
HCl	− 111°	− 83°	+ 22,000 cal.	+ 39,400 cal.
HBr	− 86°	− 69°	+ 8,600 cal.	+ 28,600 cal.
HI	− 51°	− 36°	− 6,400 cal.	+ 13,200 cal.

It will be noticed that hydrogen fluoride shows an abnormally high melting-point and boiling-point in comparison with the other hydrides of the series; in view of the fact that even the vapour of hydrogen fluoride contains molecules larger than H_2F_2, the abnormal properties of the liquid can obviously be explained by the formation of complex molecules, *e.g.*, H_2F_2, H_3F_3, etc., compare H_2O, H_4O_2, H_6O_3.

The four hydrides dissolve in water to form acids, namely, *hydrofluoric, hydrochloric, hydrobromic,* and *hydriodic acids.* These acids, which contain hydrogen, and not oxygen, in combination with a non-metal, were described by Gay-Lussac in 1814 as HYDRO-ACIDS, in order to distinguish them from OXY-ACIDS, such as sulphuric acid and chloric acid, in which oxygen is the acidifying element.

(d) *Combination with Oxygen.*—Whilst the affinity of the halogens for hydrogen diminishes progressively from fluorine to iodine, their

affinity for oxygen increases regularly in the series fluorine, chlorine, iodine. Thus,

(i) *Fluorine* does not combine with oxygen.

(ii) *Chlorine* forms three oxides, but these can only be prepared by indirect methods, and two of them are so unstable as to be definitely explosive, even when no reducing agent is present.

(iii) *Iodine* can be oxidised directly by boiling with nitric acid, and forms a remarkable series of iodates and complex periodates for which no close analogy can be found amongst the other halogens.

Bromine is anomalous in that it appears to have less affinity for oxygen than chlorine, since no oxides of bromine and no perbromates are known. The reality of this anomaly is seen in the following thermochemical data:

Compound.	*Formula.*	*Heat of formation.*
Chloric acid .	$HClO_3$ aq	+ 23,000 calories
Bromic acid .	$HBrO_3$ aq	+ 12,500 calories
Iodic acid .	HIO_3 aq	+ 56,000 calories

The general conclusion is that fluorine and bromine have less affinity for oxygen than chlorine and iodine, the alternate members of this group of elements.

Evidence of the contrast between the affinity of the halogens for hydrogen and the metals on the one hand, and for oxygen and the non-metals on the other, is found in the fact that whilst chlorine will displace iodine from potassium iodide to form potassium chloride,

$$2KI + Cl_2 = 2KCl + I_2,$$

iodine when heated with potassium chlorate will displace chlorine and form potassium iodate,

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2.$$

In the last equation the two salts may be formulated, in accordance with Lavoisier's theory, as K_2O,Cl_2O_5 and K_2O,I_2O_5, and the displacement of chlorine by iodine may be represented by the equation

$$Cl_2O_5 + I_2 = I_2O_5 + Cl_2.$$

Abnormal Properties of Fluorine.

In several respects the properties of fluorine and its compounds are anomalous in comparison with those of the other halogens and show an abrupt contrast rather than a steady gradation in properties. Thus, calcium fluoride is an insoluble mineral, whilst the chloride, bromide, and iodide are soluble deliquescent salts; and, by way of contrast, silver fluoride is soluble in water, whilst the chloride, bromide, and iodide are insoluble. Again, hydrogen fluoride in its readiness to polymerise and in its tendency to form additive compounds with

neutral salts, *e.g.*, KHF_2 (compare KHO), resembles water rather than hydrogen chloride; silicon tetrafluoride, SiF_4 (p. 489), likewise shows a curious similarity to carbon dioxide in its physical properties. The double fluorides, *e.g.*, potassium silicifluoride, K_2SiF_6, also show a much closer analogy to the corresponding oxygen compounds—*e.g.*, potassium silicate, K_2SiO_3—than is seen in the case of the chlorides. A similar analogy is seen on comparing topaz, $(AlF_2)AlSiO_4$ (p. 514), with the corresponding oxygen compound, $(AlO)AlSiO_4$, three forms of which are found as sillimanite, andalusite, and kyanite (p. 662). Finally, the direct union of carbon with fluorine corresponds with its behaviour towards oxygen, but is in marked contrast with its total resistance to attack by other halogens.

9. Fluorine. F = 19·0.

Occurrence.

Fluorine is present to the extent of about 0·1 per cent. in deep-seated igneous rocks, in which it is more abundant than chlorine. It crystallises out at a very early stage (after zircon, $ZrSiO_4$, but before any of the mineral silicates) in the form of APATITE, $Ca_5(PO_4)_3F$. These rocks retain their fluorine (just as they retain combined water) only when they crystallise under pressure; lavas, therefore, do not contain compounds of fluorine, but these are plentiful in volcanic gases, and it is suggested that mineral fluorides have been formed mainly by PNEUMOLYTIC ACTION (Greek, πνεῦμα, air or wind, λύσις, a loosening), *i.e.*, by the action of volcanic gases, on primary igneous rocks, or on secondary rocks such as chalk, $CaCO_3$, or bauxite, Al_2O_3, aq. This view finds support in the association, in mineral veins running through granite rocks, of the fluoriferous minerals, topaz, tourmaline, apatite, mica, and fluorspar.

The two most important mineral fluorides are FLUORSPAR (Latin, *fluere*, to flow; Old English, *spaer*, chalk), or **calcium fluoride,** CaF_2 (Fig. 125), and CRYOLITE (Greek, κρύος, ice; λίθος, stone), or **sodium aluminofluoride,** Na_3AlF_6 (Fig. 240), two minerals which bear in their names the record of their low melting-points. Fluorspar is a common constituent of mineral veins, where it occurs as an alternative to calcite, barytes, or quartz; it melts about 1230° (pure calcium fluoride melts at 1380°), and is used in metallurgy as a flux to protect metals from atmospheric oxidation or to increase the fluidity of a slag. Cryolite, of which important deposits are found in Iceland, is used as a solvent for bauxite in the manufacture of aluminium. Topaz, $(AlF_2)AlSiO_4$, and the mica known as lepidolite (p. 505) also contain fluorine in combination with aluminium.

Isolation of Fluorine.

(*a*) *Preparation of Fluorine.*—Davy attempted to isolate fluorine by passing an electric current through hydrofluoric acid; but as fluorine

attacks carbon, water, and most of the metals with extreme violence, he did not succeed in separating the element. Fluorine was therefore unknown in the elementary state until it was isolated by Moissan in 1886, by passing an electric current through an anhydrous mixture of hydrogen fluoride and potassium fluoride.

The electrolysis was carried out in a platinum U-tube, Fig. 126, cooled to − 23°, by the evaporation of methyl chloride. The electrodes, *tt*, of platinum-iridium alloy, were insulated from the U-tube by stoppers, *FF*, of fluorspar, the joints being made air-tight by leaden washers, *p*, screwed down by brass caps, *E*. Hydrogen was liberated at the negative and fluorine at the positive electrode. This apparatus has recently been developed for the manufacture of fluorine as a laboratory product, by the electrolysis of fused potassium hydrogen fluoride, KHF_2, between a copper cathode and a graphite anode.

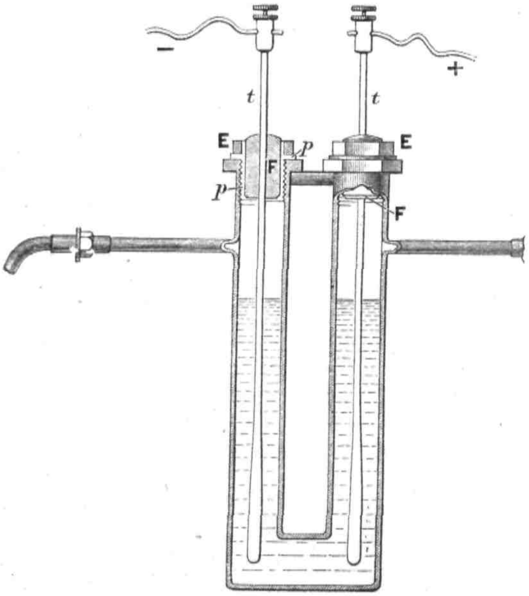


FIG. 126.—MOISSAN'S APPARATUS FOR THE PREPARATION OF FLUORINE.

(*b*) *Physical Properties of Fluorine.*—Fluorine is a light yellow gas, condensing to a liquid at − 187°, and crystallising to a pale yellow solid melting at − 233°.

(*c*) *Chemical Properties of Fluorine.*—Fluorine is a very active gas. It unites explosively with hydrogen even at − 253°. It decomposes water at once, forming hydrofluoric acid and liberating oxygen in the form of ozone. It ignites charcoal, combines vigorously with phosphorus, liberates chlorine from potassium chloride, and unites directly with nearly all the metals, although gold fluoride, AuF_3, and platinum fluoride, PtF_4, are no longer stable at a red heat; but it has no marked action on dry glass, and does not combine with oxygen.

In its general properties fluorine shows many marked points of resemblance to oxygen, but its activity is greater even than that of ozone, and may perhaps be regarded as indicating the extreme activity

that would probably be found in oxygen if it could be obtained in the form of single atoms.

Hydrogen Fluoride.

(*a*) *Preparation.*—Hydrogen fluoride is liberated from fluorspar, just as hydrogen chloride is liberated from common salt, by the action of concentrated sulphuric acid.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF;$$

compare $$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The acid has been known since 1670, but it was not until 1813 that Davy recognised in fluorspar and its acid the presence of an element resembling chlorine, which he proposed to call FLUORINE.

As hydrofluoric acid attacks glass, it must be distilled in retorts of silver or lead and collected in receivers of the same metal. Since it cannot be stored in glass bottles, rubber or wax (ceresin) flasks and stoppers are commonly used.

The acid obtained by distillation contains water. The anhydrous acid, as used by Moissan in isolating elementary fluorine, is prepared from the acid salt, KHF_2, which is melted to remove all traces of water and decomposed by heating to redness in a platinum retort; this is connected to a platinum condenser and receiver, the latter being cooled with a freezing mixture to condense the acid. The last traces of moisture are only removed during the early stages of electrolysis, when ozone is set free instead of fluorine. The anhydrous acid is dangerous to handle, as the liquid blisters the skin and inhalation of the vapour may have a fatal effect. The anhydrous acid, unlike commercial hydrofluoric acid, destroys rubber bottles but does not attack glass.

(*b*) *Physical Properties.*—Anhydrous hydrogen fluoride has a density of 0·987 at 13° and is therefore very slightly lighter than water; it boils at 19·5° and freezes at −92°. Like hydrogen chloride, it dissolves freely in water and forms a mixture of constant boiling-point; this contains 37 per cent. of hydrogen fluoride and boils at 120°.

The vapour density of hydrogen fluoride at temperatures above 70° corresponds with that required by the formula HF; but already at 27° the relative density of the vapour has become about 2·5 times as great, so that the liquid probably contains molecules not less complex than H_3F_3. The polymerisation of the simple molecules, and the abnormally high boiling-point and freezing-point which result from this polymerisation, bring hydrogen fluoride into the same class of compounds as water and provide a further analogy between fluorine and oxygen.

(*c*) *Metallic Fluorides.*—Hydrogen fluoride is an acid which forms a series of FLUORIDES by acting on metals or their oxides. The fluorides

are analogous with the chlorides; but calcium fluoride is an insoluble mineral, whilst calcium chloride, bromide, and iodide are soluble deliquescent salts; and conversely silver fluoride is soluble in water, whilst silver chloride, bromide, and iodide are insoluble. Many of the metallic fluorides will combine with a further quantity of hydrogen fluoride to form acid fluorides,

$$KF + HF = KHF_2;$$

compare $$K_2O + H_2O = 2KHO.$$

(*d*) *Action on Silica and Etching of Glass.*—Hydrogen fluoride attacks silica, with the formation of silicon tetrafluoride and water:

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

The use of hydrofluoric acid in etching glass depends upon this action of the acid upon the silica in the glass; the glass is coated with wax, the lines which are to be etched are scratched with a metal point to remove the wax, and the plate is then exposed to the action of the vapour during a period of several hours. This action is also used in estimating silica, *e.g.*, in minerals or in slags, by volatilisation in presence of hydrogen fluoride.

(*e*) *Double Fluorides.*—The action shown above is a balanced one, which is reversed by the addition of water. The fluorine is, however, set free, not as hydrofluoric acid, but in the form of a **silicifluoric** or **fluosilicic acid,** H_2SiF_6 (compare H_2SiO_3):

$$\underset{\text{Silicon tetrafluoride.}}{3SiF_4} + 4H_2O = \underset{\text{Silicifluoric acid}}{2H_2SiF_6} + \underset{\text{Silicic acid}}{Si(OH)_4}.$$

From this acid a series of SILICIFLUORIDES * or FLUOSILICATES is derived, *e.g.*,

Potassium silicifluoride, K_2SiF_6,
Lead silicifluoride, $PbSiF_6$.

These compounds are typical of a long series of DOUBLE FLUORIDES in which fluorine resembles oxygen in combining both with a metal and with a non-metal, forming a pair of fluorides which unite to form a salt, just as oxy-salts are formed by the union of a basic oxide with an acid oxide. Amongst these double fluorides are:

Potassium borifluoride,	KBF_4.
Potassium titanifluoride,	K_2TiF_6.
Potassium germanifluoride,	K_2GeF_6, isomorphous with
ammonium silicifluoride,	$(NH_4)_2SiF_6$.
Potassium zirconifluoride,	K_2ZrF_6,
Potassium plumbifluoride,	K_2PbF_6,KHF_2
Potassium thorifluoride,	K_2ThF_6.

* These are also known as silic*o*fluorides, but the name given in the text is to be preferred as corresponding more closely with the quadrivalent compounds of germanium, tin, lead, etc.

Detection and Estimation of Fluorine.

(*a*) *Detection.*—The most delicate test for compounds of fluorine depends upon the etching of glass by hydrofluoric acid set free by warming the substance with concentrated sulphuric acid ; one part of fluorine in five million parts can be detected by this method. When the substance contains silica in addition to fluorine, silicon fluoride is evolved and can be detected by the white deposit of silicic acid which it gives on a drop of water held in the vapours.

(*b*) *Estimation.*—Fluorine is usually estimated by bringing it into solution as an alkali fluoride, precipitating it as calcium fluoride by adding an excess of calcium chloride, and igniting the precipitate at a low red heat. A more rapid method of estimation consists in heating the substance with strong sulphuric acid and silica and measuring the volume of silicon fluoride evolved.

(*c*) *Atomic weight.*—The accepted value for the atomic weight of fluorine is based mainly upon the conversion of fluorides into sulphates, *e.g.*, $CaF_2 : CaSO_4$; $2NaF : Na_2SO_4$; $2KF : K_2SO_4$.

35. Bromine. Br = 79·92.

Occurrence of Bromine.

Bromine is present in small quantities in sea-water and is found in the upper layers of the salt-beds in which the magnesium salts are concentrated ; as these upper layers are only preserved in the potash-bearing mines, the supply of bromine is controlled by the holders of the potash deposits.

Preparation of Bromine.

Bromine was discovered in 1826 by Balard, who obtained the element in the form of a dark red liquid by condensing the red vapours which are set free on distilling the mother liquors of sea-water after passing in chlorine,

$$Cl_2 + 2KBr = Br_2 + 2KCl.$$

The element had already been separated in this way by Liebig, but he had labelled his specimen "chloride of iodine," and did not recognise that he was handling a new element.

Bromine is prepared commercially by passing chlorine from the plant *D* (Fig. 127) into the bottom of a tower, *A*, down which the mother liquors from the preparation of potassium and magnesium salts are allowed to flow. The spent liquors flowing from the tower at *d* are freed from bromine and chlorine by blowing superheated steam into them as they flow down a second column, *B*, the vapours being carried back into the tower through the wide pipe, *d*. The bromine escaping as vapour at the top of the tower, *A*, is condensed to a liquid at *p*, and the last traces of chlorine and bromine are removed by wet iron-filings

after adding a suitable quantity of a metallic bromide, *e.g.*, KBr or $FeBr_2$. Final purification from the last traces of chlorine and iodine

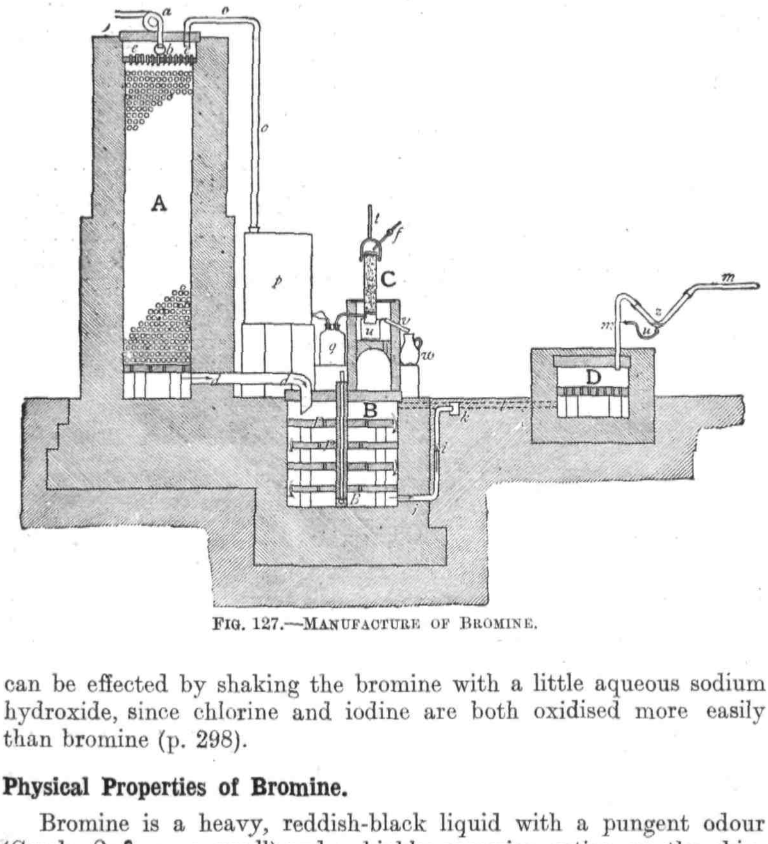


FIG. 127.—MANUFACTURE OF BROMINE.

can be effected by shaking the bromine with a little aqueous sodium hydroxide, since chlorine and iodine are both oxidised more easily than bromine (p. 298).

Physical Properties of Bromine.

Bromine is a heavy, reddish-black liquid with a pungent odour (Greek, βρῶμος, a smell) and a highly corrosive action on the skin. Its density is 3·12 at 20°. It is the only non-metallic element that is liquid at normal atmospheric temperatures, just as mercury is the only metal which is normally a liquid. Liquid bromine boils at 58·6° and freezes at — 7·3° ; the crystals are reddish-brown, but become colourless when cooled to — 253° by liquid hydrogen. Bromine mixes in all proportions with chloroform and ether, but forms two layers with water ; the upper aqueous layer consists of BROMINE-WATER and contains 3·6 per cent. of bromine at 10°, whilst the lower layer contains only about 0·04 per cent. of water ; this water can be removed by distilling the bromine from sulphuric acid. Below 3·5° aqueous solutions of bromine deposit the crystalline hydrate, $Br_2,10H_2O$, instead of liquid bromine (compare chlorine, p. 273).

Chemical Properties of Bromine.

(*a*) *Addition.*—Bromine combines directly with hydrogen, and with sulphur and phosphorus, but not with carbon, oxygen, or nitrogen. Like chlorine it unites with metals, forming BROMIDES (see below), which are usually salt-like in their properties. It also combines with a large number of "unsaturated compounds," *e.g.*,

$$C_2H_4 + Br_2 = C_2H_4Br_2 \text{ (ethylene bromide)},$$
$$C_2H_2 + 2Br_2 = C_2H_2Br_4 \text{ (acetylene tetrabromide)}.$$

(*b*) *Substitution.*—Bromine will displace hydrogen from organic compounds such as benzene,

$$C_6H_6 + 2Br_2 = C_6H_4Br_2 + 2HBr,$$

sulphur from carbon disulphide and sulphuretted hydrogen,

$$CS_2 + 2Br_2 = CBr_4 + S_2$$
$$H_2S + Br_2 = 2HBr + S,$$

and iodine from hydriodic acid and metallic iodides,

$$2HI + Br_2 = 2HBr + I_2$$
$$2KI + Br_2 = 2KBr + I_2$$

Hydrogen Bromide.

(*a*) *Combination of Hydrogen and Bromine.*—Hydrogen and bromine unite together when heated, *e.g.*, hydrogen bromide is formed when hydrogen is bubbled through liquid bromine and then ignited or passed over red-hot platinum. This action is reversible,

$$H_2 + Br_2 \rightleftharpoons 2HBr,$$

but is practically complete when a slight excess of hydrogen is used, as dissociation of hydrogen bromide only takes place to the extent of about 1 per cent. even at 1200°.

The combination is exothermic:

$$H_2 + Br_2 \text{ (liq.)} = 2HBr \text{ (gas)} + 2 \times 8{,}600 \text{ cal.}$$
$$H_2 + Br_2 + Aq = 2HBr, aq + 2 \times 28{,}600 \text{ cal.}$$

(*b*) *Oxidation of Hydrogen Bromide.*—As the heat of formation of hydrogen bromide, even in aqueous solution, is much less than the heat of formation of water, hydrogen bromide is readily oxidised, with liberation of bromine:

$$\underset{4 \times 28{,}600}{4HBr, aq} + O_2 = \underset{2 \times 68{,}360}{2H_2O} + 2Br_2 \text{ (liq.)} + 22{,}320 \text{ cal.}$$

For this reason it cannot be prepared in the same way as hydrogen fluoride and hydrogen chloride, since, when sulphuric acid acts upon a bromide, bromine and sulphur dioxide are also produced:

$$2KBr + 2H_2SO_4 = K_2SO_4 + Br_2 + SO_2 + 2H_2O.$$

This is a balanced action, since, although heating with strong sulphuric

acid liberates bromine and sulphur dioxide from potassium bromide, bromine and sulphur dioxide interact in aqueous solutions to form hydrobromic and sulphuric acids,

$$Br_2 + 2H_2O + SO_2 = 2HBr + H_2SO_4.$$

(c) *Preparation of Hydrogen Bromide.*—Aqueous hydrobromic acid can be prepared very conveniently by reducing the halogen under water by the action of sulphur dioxide, as shown in the preceding equation. On heating the solution, aqueous hydrobromic acid distils, whilst the sulphuric acid remains behind. Hydrogen bromide can be prepared in a gaseous form by the action of sulphuretted hydrogen on bromine,

$$Br_2 + H_2S = 2HBr + S,$$

or by the combined action of red phosphorus and water,

$$5Br_2 + 8H_2O + 2P = 10HBr + 2H_3PO_4 ;$$

it is also formed as a by-product in the bromination of many organic compounds, *e.g.*,

$$\underset{\text{Naphthalene}}{C_{10}H_8} + Br_2 = \underset{\text{Bromonaphthalene}}{C_{10}H_7Br} + HBr.$$

$$\underset{\text{Camphor}}{C_{10}H_{16}O} + Br_2 = \underset{\text{Bromocamphor}}{C_{10}H_{15}BrO} + HBr.$$

The gas set free by any of these methods may be freed from bromine by passing it over red phosphorus, and then absorbed in water.

(d) *Physical Properties of Hydrogen Bromide.*—Hydrogen bromide is a colourless gas which fumes in the air. It condenses to a liquid which boils at − 69° and freezes at − 86°. It dissolves freely in water and gives a mixture of maximum boiling-point containing 48 per cent. of HBr and boiling at 125°.

By cooling its aqueous solutions, hydrates with $1H_2O$ (under pressure only), $2H_2O$, $3H_2O$, and $4H_2O$ can be crystallised out at temperatures ranging from − 3° downwards. Above − 3° (under pressure) two liquid layers are formed, the upper aqueous layer containing 79 per cent. of HBr at −3°, whilst the lower layer of hydrogen bromide contains very little water.

(e) *Chemical Properties of Hydrogen Bromide.*—Hydrogen bromide dissolves in water to form an acid, from which a series of metallic BROMIDES can be prepared; these can also be made by direct combination of bromine with the metals, although in some instances this gives rise to higher bromides than those prepared by the action of hydrogen bromide, *e.g.*,

$$Sn + 2HBr = \underset{\text{Stannous bromide}}{SnBr_2} + H_2. \qquad Fe + 2HBr = \underset{\text{Ferrous bromide}}{FeBr_2} + H_2.$$

$$Sn + 2Br_2 = \underset{\text{Stannic bromide}}{SnBr_4}. \qquad 2Fe + 3Br_2 = \underset{\text{Ferric bromide}}{2FeBr_3}.$$

Amongst the bromides of the metals, **potassium bromide**, KBr, is used in medicine as a sedative, whilst **silver bromide**, AgBr, is important in analysis on account of its insolubility.

As described under (*b*) above, hydrobromic acid is very readily oxidised, with liberation of bromine, but is not sufficiently active to be regarded as a reducing agent.

Action of Bromine on Alkalies. Hypobromous and Bromic Acids.

By the action of bromine on aqueous potassium hydroxide in the cold, potassium bromide and **potassium hypobromite**, KBrO, are produced:

$$Br_2 + 2KOH = KBr + KBrO + H_2O.$$

The solution has bleaching and oxidising properties, but changes even more readily than the hypochlorite, giving a mixture of potassium bromide and **potassium bromate**, $KBrO_3$,

$$3KBrO = 2KBr + KBrO_3;$$

compare $$3KClO = 2KCl + KClO_3.$$

The production of the bromate by the action of bromine on potassium hydroxide may be shown by a single equation as follows:

$$3Br_2 + 6KOH = 5KBr + KBrO_3 + 3H_2O;$$

compare $$3Cl_2 + 6KOH = 5KCl + KClO_3 + 3H_2O.$$

Hypobromous acid, HBrO, can be prepared by the action of bromine on mercuric oxide,

$$2Br_2 + HgO + H_2O = HgBr_2 + 2HBrO.$$

The chemical change is similar to that which takes place when bromine acts on potassium hydroxide, but hypobromous acid (like hypochlorous acid) is too weak an acid to be held by mercuric oxide and is therefore obtained in the free state. The acid forms a yellow solution and resembles hypochlorous acid in its oxidising and bleaching properties.

Bromic acid, $HBrO_3$, can be prepared by converting potassium bromate into silver bromate by the addition of silver nitrate, and then precipitating the silver, *e.g.*, by means of bromine water; this has the advantage over hydrobromic acid of producing an additional molecule of bromic acid as shown in the equation

$$5AgBrO_3 + 3Br_2 + 3H_2O = 5AgBr + 6HBrO_3.$$

Bromic acid is also formed as a main product of the action of chlorine on bromine water,

$$Br_2 + 5Cl_2 + 6H_2O = 10HCl + 2HBrO_3,$$

whereas, in the absence of bromine, the analogous change represented by the equation

$$3Cl_2 + 3H_2O = 5HCl + HClO_3$$

only takes place to a very slight extent in the absence of alkalies.

Bromic acid, like chloric acid, can be concentrated by evaporating in a vacuum, but the solution decomposes when heated; as the oxides of bromine are too unstable to be isolated, this decomposition leads to the production of free bromine and oxygen, where chloric acid yields chlorine dioxide.

Bromic acid is reduced by sulphur dioxide and by sulphuretted hydrogen:

$$HBrO_3 + 3SO_2 + 3H_2O = 3H_2SO_4 + HBr;$$
$$HBrO_3 + 3H_2S = 3H_2O + 3S + HBr.$$

It is also reduced by hydrogen bromide, this action being a reversal of that which takes place when bromine acts upon potash,

$$5HBr + HBrO_3 = 3Br_2 + 3H_2O.$$

53. Iodine. I = 126·92.

Occurrence.

Iodine is present in sea-water, but only in minute quantities. It is, however, absorbed by marine plants and can be manufactured from the ash of seaweed, to which the name of KELP is given; the ash from some species of seaweed contains over 1 per cent. of iodine, but this may be reduced to ½ per cent. or less by over-burning.

Iodine was discovered in 1811 by Courtois, who heated with sulphuric acid the mother liquors of kelp from which sodium carbonate had crystallised, and obtained a beautiful violet vapour which condensed to black, lustrous crystals. The name of iodine was given to it on account of the violet colour of its vapour (Greek, ἰώδης, violet).

The nitrate beds of Chile also contain iodine, mainly in the form of sodium iodate, and large quantities of iodine could be obtained from this source if required.

Preparation of Iodine.

(*a*) *From Kelp.*—After extracting with water and crystallising out potassium sulphate, potassium chloride, and common salt, the mother liquor is mixed with sulphuric acid, separated from sulphur (derived from sulphides formed in burning the ash), and distilled with manganese dioxide from iron pots into a series of earthenware condensers,

$$2NaI + 3H_2SO_4 + MnO_2 = I_2 + 2NaHSO_4 + MnSO_4 + 2H_2O.$$

As an alternative, the iodine can be precipitated by the action of chlorine,

$$2NaI + Cl_2 = I_2 + 2NaCl.$$

(*b*) *From Caliche or Crude Sodium Nitrate.*—The iodine is present in the mother liquors in quantities up to 0·3 per cent. in the form of sodium iodate, $NaIO_3$. It is therefore separated, not by oxidation, but by reduction with crude sodium bisulphite,

$$2NaIO_3 + 5NaHSO_3 = I_2 + 2Na_2SO_4 + 3NaHSO_4 + H_2O.$$

(*c*) *Purification.*—The crude iodine is purified by sublimation, if necessary after adding potassium iodide in order to eliminate other halogens. The cyanide, ICN, is a dangerous impurity which may appear as colourless crystals in the first portions of the sublimate from kelp.

Properties of Iodine.

Iodine forms brilliant black crystals with a lustre that is almost metallic. The density of the solid is 4·94. It melts at 113° and boils at 184°; but its vapour-pressure at the melting-point is so high that it readily sublimes without melting.

The vapour-density of iodine at low temperatures corresponds with the formula I_2, but marked dissociation takes place when the temperature is raised, the calculated proportions of the two constituents being as follows:

TABLE 39.—DISSOCIATION OF IODINE.

	I_2 $\rightleftharpoons$	2I.	
At 400°	99·94 %	0·06%	
At 600°	95·3	4·7	or 20 : 1
At 800°	89·5	10·5	or 9 : 1
At 1000°	62	38	or 5 : 3
At 1200°	26	74	or 1 : 3.

It is only slightly soluble in water (1 part in 5000), but dissolves freely in carbon disulphide and in chloroform, giving violet solutions, and in alcohol and in aqueous potassium iodide, giving brown solutions,

$$KI + I_2 = KI_3.$$

Chemical Properties of Iodine.

(*a*) *Iodine and the Non-metals.*—Iodine and hydrogen unite to form hydrogen iodide (see below). Iodine also unites directly with chlorine to form the iodides, ClI and Cl_3I (Fig. 121*b*, p. 277). With bromine it gives a compound, BrI, which forms isomorphous crystals, on the one hand with iodine and on the other with bromine (Fig. 128). With fluorine it forms a pentafluoride, IF_5. It unites with phosphorus to form the iodides, PI_3 and P_2I_4, but gives only an eutectic with sulphur. It can be oxidised to the pentoxide, I_2O_5, and will displace hydrogen

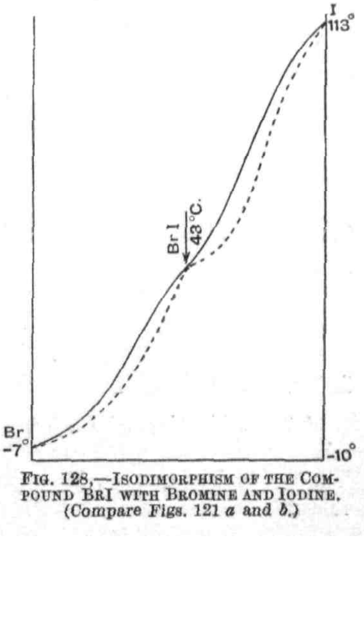


FIG. 128.—ISODIMORPHISM OF THE COMPOUND BRI WITH BROMINE AND IODINE. (Compare Figs. 121 *a* and *b*.)

in ammonia to form an explosive nitrogen iodide, but it has no action upon gaseous oxygen or nitrogen, nor upon carbon.

(*b*) *Iodine and the Metals.*—Iodine unites directly with metals to form a series of IODIDES which resemble the chlorides in their general properties, but are frequently coloured even when the corresponding chlorides and bromides are colourless. Thus, when mercury and iodine are rubbed together a green **mercurous iodide**, Hg_2I_2, is formed when the mercury is in excess, and a red **mercuric iodide**, HgI_2, when the iodine is in excess :

$$2Hg + I_2 = Hg_2I_2$$
$$Hg + I_2 = HgI_2.$$

It is noteworthy that whilst copper forms two chlorides, Cu_2Cl_2 and $CuCl_2$, cupric iodide is unstable and breaks down at once into cuprous iodide and iodine,

$$\underset{\text{Cupric iodide}}{2CuI_2} = \underset{\text{Cuprous iodide}}{Cu_2I_2} + I_2 ;$$

since chlorine and bromine do not behave in this way, very pure iodine can be prepared by precipitating it as cuprous iodide, drying, and heating in a current of oxygen to liberate the iodine. Iodine also differs from chlorine in forming metallic PERIODIDES, *e.g.*,

$$KI + I_2 = KI_3 ;$$

with cæsium iodide, compounds up to CsI_5 have been isolated.

(*c*) *Iodine as an Oxidising Agent.*—Iodine is a useful oxidising agent, although less powerful than chlorine. It oxidises sulphuretted hydrogen,

$$I_2 + H_2S = 2HI + S,$$

and will remove sodium from compounds containing the group —SNa, converting them into disulphides containing the group —S·S—, *e.g.*,

$$I_2 + \underset{\text{Sodium thiosulphate}}{2NaS{\cdot}SO_2{\cdot}ONa} = 2NaI + \underset{\text{Sodium tetrathionate}}{\begin{array}{c}S{\cdot}SO_2{\cdot}ONa \\ | \\ S{\cdot}SO_2{\cdot}ONa\end{array}},$$

just as chlorine oxidises potassium manganate to potassium permanganate,

$$Cl_2 + \underset{\text{Potassium manganate}}{2K_2MnO_4} = 2KCl + \underset{\text{Potassium permanganate}}{2KMnO_4}.$$

Iodine and Hydrogen.

(*a*) *Combination of Hydrogen and Iodine.*—Iodine unites directly with hydrogen when the gas and vapour are passed through a hot tube. The action is, however, incomplete, the equilibrium being roughly as follows :

TABLE 40.—DISSOCIATION OF HYDROGEN IODIDE.

	$2HI$	$\rightleftharpoons H_2 + I_2$.
At 300°	82%	18%
At 400°	80	20
At 500°	76	24

As the dissociation of the iodide is not accompanied by change of volume, pressure has no important influence on the equilibrium.

The heat of formation of the gas is negative,

$$H_2 \text{ (gas)} + I_2 \text{ (solid)} = 2HI \text{ (gas)} - 2 \times 6400 \text{ cal.},$$

but it becomes positive in presence of water,

$$H_2 \text{ (gas)} + I_2 \text{ (solid)} + Aq = 2HI, aq + 2 \times 13{,}200 \text{ cal.}$$

As the latent heat of sublimation of iodine is about 15,000 calories per gram-molecule, the heat of formation of hydrogen iodide is also positive when *gaseous* iodine and gaseous hydrogen unite to form gaseous hydrogen iodide,

$$H_2 \text{ (gas)} + I_2 \text{ (vapour)} = 2HI \text{ (gas)} + 2 \times 1100 \text{ cal.};$$

the dissociation of the iodide therefore increases with rising temperature, as in the case of other exothermic compounds.

(*b*) *Preparation of Hydrogen Iodide.*—Hydrogen iodide cannot be prepared by the action of sulphuric acid on potassium iodide, since oxidation takes place to an even larger extent than in the case of the bromide,

$$2KI + 3H_2SO_4 = 2KHSO_4 + I_2 + SO_2 + 2H_2O.$$

This oxidation (like that of hydrogen bromide) is a balanced action, since in aqueous solutions iodine is decolorised immediately by sulphur dioxide. Sulphuretted hydrogen is also produced by the action of strong sulphuric acid on potassium iodide, thus,

$$8KI + 9H_2SO_4 = 8KHSO_4 + 4I_2 + H_2S + 4H_2O.$$

In order to get over this difficulty, hydrogen iodide is usually prepared by the reduction of iodine, either by sulphuretted hydrogen,

$$I_2 + H_2S = 2HI + S,$$

or by phosphorus in presence of water,

$$P_4 + 10I_2 + 16H_2O = 20HI + 4H_3PO_4.$$

The former method is convenient for preparing dilute solutions, but the action tends to reverse at high concentrations; the latter method can be used to prepare gaseous hydrogen iodide by mixing together water, phosphorus, and iodine in suitable proportions and warming the mixture to expel the gas.

(*c*) *Physical Properties.*—Hydrogen iodide is a gas which fumes in the air and condenses to a heavy liquid of density 2·8, which boils at − 36° and freezes at − 51°. It dissolves freely in water and gives an acid of maximum boiling-point which contains 58 per cent. of

hydrogen iodide and boils at + 127°. By strongly cooling its solution hydrates with $3H_2O$ and $4H_2O$ can be crystallised out.

(*d*) *Hydrogen Iodide as a Reducing Agent.*—In addition to exhibiting acid properties when dissolved in water to form hydriodic acid, hydrogen iodide can act also as a reducing agent, since the hydrogen which it contains is held only very loosely. In this respect it resembles hydrogen sulphide (p. 324). Ozone, hydrogen peroxide, and persulphuric acid will liberate iodine even from potassium iodide; but the greater reducing power of the free acid is seen in its action upon sulphuric acid, to which reference has already been made. The reduction of iodic acid by hydrogen iodide is referred to below.

Concentrated solutions of hydrogen iodide, heated in a sealed tube to prevent escape of gas, are widely used as reducing agents in organic chemistry, especially in those cases in which it is desired to replace a hydroxyl-group by hydrogen; in this case the hydrogen iodide probably acts first as an acid to convert the hydroxide into an iodide,

$$ROH + HI = RI + H_2O,$$

and then as a reducing agent in replacing the iodine by hydrogen,

$$RI + HI = RH + I_2;$$

this action can be carried out more efficiently when red phosphorus is added to combine with the iodine as it is formed.

Iodine and Oxygen.

Iodine forms the following compounds:

Oxide.	*Oxy-acids.*
Iodine dioxide, IO_2.	Hypoiodous acid, HIO
Iodine pentoxide, I_2O_5	Iodic acid, HIO_3
—	Periodic acids, HIO_4, H_3IO_5, H_5IO_6, etc.

Iodine and the Alkalies.

When iodine is dissolved in cold potash, potassium iodide and **potassium hypoiodite**, KIO, are formed:

$$I_2 + 2KOH = KI + KIO + H_2O.$$

This action differs from the corresponding action in the case of chlorine (i) in that it is reversible, the iodine being only partly combined; (ii) in that the further conversion to IODATE as indicated in the equation

$$3I_2 + 6KOH = 5KI + KIO_3 + 3H_2O$$

takes place gradually even in cold solutions.

When this mixture of iodide and iodate is acidified there is a quantitative liberation of iodine as shown in the equation

$$5HI + HIO_3 = 3I_2 + 3H_2O.$$

This action can be used for the estimation of acids, since each equivalent of acid liberates one equivalent of iodine, which can then be estimated by titration as described below.

The solution of iodine in potash and its liberation by means of acids may be compared with the preparation of liver of sulphur and the reprecipitation of the sulphur in the form of milk of sulphur. In each case the non-metal can form an acid by combination both with hydrogen and with oxygen, with the result that, in presence of an alkali, water is decomposed and salts derived from the acid hydride and from the acid oxide are produced. When, however, the acids are released from combination with the alkali, water is formed again and the non-metal is set free.

$$3I_2 + 3H_2O \underset{Acid}{\overset{Alkali}{\rightleftarrows}} 5HI + HIO_3.$$

$$3S + 2H_2O \underset{Acid}{\overset{Alkali}{\rightleftarrows}} 2H_2S + SO_2.$$

Oxides and Oxy-acids of Iodine.

Hypoiodous acid, HIO, is formed by the action of mercuric oxide on iodine suspended in water,

$$2I_2 + HgO + H_2O = HgI_2 + 2HIO.$$

Iodine dioxide, IO_2 or I_2O_4, compare nitrogen peroxide (p. 413), is formed by grinding iodine with cold concentrated nitric acid of density 1·5; the product contains nitrogen, but on standing over lime leaves a residue of the oxide. This is a yellow, amorphous powder, which decomposes at 170–180° into iodine and iodic anhydride, whilst with boiling water it gives iodine and iodic acid. It acts as a base towards sulphuric acid; thus a crystalline **sulphate**, $(IO_2)H_2SO_4$, separates when a solution of the oxide in strong sulphuric acid is cooled.

Iodic acid, HIO_3, is formed

(i) By dissolving iodine in nitric acid,

$$3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O.$$

(ii) By oxidising iodine with chlorine water,

$$I_2 + 5Cl_2 + 6H_2O = 10HCl + 2HIO_3;$$
$$\text{compare } 3Cl_2 + 6KOH = 5KCl + KClO_3 + 3H_2O;$$

the hydrochloric acid can be removed by shaking with silver oxide.

(iii) From barium iodate and sulphuric acid (compare chloric acid).

Iodic acid is a heavy crystalline solid, which dissolves in water, to which it gives an acid reaction. It is a monobasic acid, but forms acid as well as neutral salts, *e.g.*, KIO_3, $KH(IO_3)_2$, $KH_2(IO_3)_3$. Above 110°

it separates from water as HIO_3,I_2O_5, and on heating to 200° is converted into **iodic anhydride**, I_2O_5, a heavy, white powder which decomposes into iodine and oxygen when heated to 300°, and has the property of oxidising carbon monoxide at 150° :

$$I_2O_5 + 5CO = I_2 + 5CO_2.$$

The oxidising action of iodic acid is similar to that of bromic acid.

Periodic acid, $HIO_4,2H_2O$, is formed from iodic acid by electrolytic oxidation; potassium periodate can also be prepared in this way from potassium iodate (compare potassium perchlorate). The anhydrous acid is not known, but salts of the types

$NaIO_4$, Na_3IO_5, Na_5IO_6, derived from HIO_4, HIO_4,H_2O, and $HIO_4,2H_2O$, and

$Na_4I_2O_9$, $Na_8I_2O_{11}$, $Na_{12}I_2O_{13}$, derived from $2HIO_4,H_2O$, $2HIO_4,3H_2O$, and $2HIO_4,5H_2O$,

have been prepared.

CHAPTER XXV

16. SULPHUR. S = 32·06.

Occurrence of Sulphur.

Sulphur and phosphorus, like fluorine and chlorine, each represent only about 0·1 per cent. of the earth's crust. The sulphur in the igneous magma separates from it in the form of PYRRHOTITE or **magnetic sulphide of iron** ($FeS + Fe_3S_4$), whereas the phosphorus crystallises out in an oxidised form as apatite, $Ca_5(PO_4)_3F$ (p. 418). Pyrrhotite is readily decomposed by steam, with the result that **sulphuretted hydrogen**, H_2S, and NATIVE SULPHUR are abundant in volcanic districts, whilst mineral veins contain METALLIC SULPHIDES (see (*b*) below) which appear to have been precipitated from deep-seated waters by the action of sulphuretted hydrogen. In contact with oxygen, sulphuric acid and MINERAL SULPHATES, in addition to free sulphur, are formed by oxidation of these sulphides, giving rise for instance to extensive deposits of GYPSUM, $CaSO_4,2H_2O$ (p. 635), formed by the metamorphosis of chalk or limestone.

(*a*) *Native sulphur* is abundant in the volcanic districts of Sicily, but even larger quantities are now obtained from the American sulphur mines in Louisiana.

(i) In Sicily the sulphur is melted out from the limestone and other rocks with which it is mixed, either by setting fire to and burning a part of the sulphur, or by using a certain amount of auxiliary fuel. The sulphur is purified by distilling it from an iron pot (Fig. 129) into a chamber in which it condenses, either as solid FLOWERS OF SULPHUR or as a liquid which is cast into sticks and sold as ROLL SULPHUR or sent out in massive blocks.

(ii) In Louisiana, the sulphur deposits are found a few hundred feet below the surface, but covered with a quicksand which prevents the use of ordinary methods of mining. The sulphur is therefore brought to the surface in a molten form by the FRASCH PROCESS, in which superheated steam is forced down one of a series of concentric pipes to melt the sulphur, whilst compressed air is used to drive up molten sulphur through another of the series of pipes. The molten sulphur is allowed to flow into very large bins, where it solidifies in masses up to 150,000 tons; the solid sulphur is then broken up by

explosives, quarried by means of "steam-navvies" and loaded into trucks.

(*b*) *Combined sulphur* is present in a large number of common mineral sulphides and sulphates, *e.g.*,

Sulphides.		*Sulphates.*	
Iron pyrites,	FeS_2	Epsom salts,	$MgSO_4,7H_2O$
Galena,	PbS	Selenite or Gypsum,	$CaSO_4,2H_2O$
Blende,	ZnS	Celestine,	$SrSO_4$
Cinnabar,	HgS	Heavy spar or Barytes,	$BaSO_4$

Iron pyrites is by far the most important ore of sulphur and is burnt on a very large scale in the manufacture of sulphuric acid ; it can also be made to yield one-third of its sulphur in an elementary form by heating it in a closed retort, as is shown by the equation :—

$$3FeS_2 = Fe_3S_4 + S_2 ;$$

compare

$$3MnO_2 = Mn_3O_4 + O_2.$$

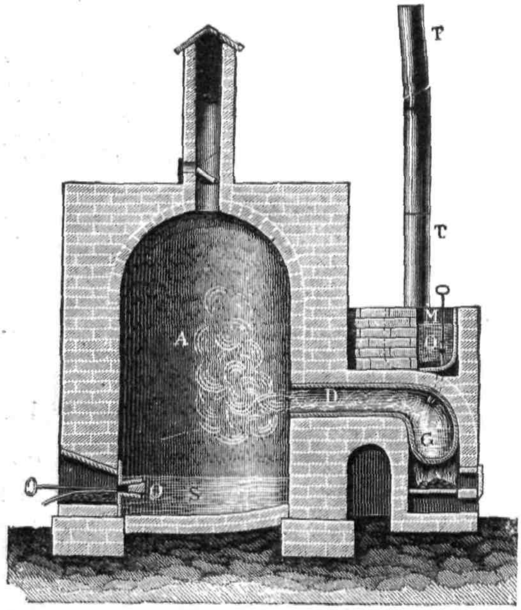


FIG. 129.—DISTILLATION OF SULPHUR.

Molten sulphur from *O* is admitted by means of a valve, *M* to the retort, *G*. The vapour escapes through *D* into the chamber, *A*, where it condenses at first as flowers of sulphur, but when the chamber is hot as liquid sulphur, *S*, which is drawn at *Q* and cast.

In recent years the sulphur dioxide produced by calcining other mineral sulphides, *e.g.*, ZnS, has been utilised in the manufacture of sulphuric acid instead of being released into the air. Attempts have also been made to utilise the sulphur present in gypsum, by substituting gypsum for chalk in the manufacture of Portland cement (p. 640) and converting into sulphuric acid the sulphur dioxide which is then set free during the burning of the clinker.

Properties of Sulphur.

(*a*) *Physical Properties.*—Sulphur is a pale yellow brittle solid, which melts at about 113° and boils at 444·6° under 760 mm. pressure.

The melting-point varies considerably with the experimental conditions, but the boiling-point is sufficiently constant to be used as a secondary standard in calibrating thermometers and pyrometers for use at high temperatures.

(*b*) *Chemical Properties.*—Sulphur unites directly with most of the metals to form SULPHIDES similar to those which are found in the native state as minerals. It burns in air or oxygen, to the oxides SO_2 and SO_3 (p. 328), unites directly with phosphorus and the halogens, and less readily with carbon and hydrogen; it is not acted upon by nitrogen. It is insoluble in acids, but dissolves in alkalies, forming "liver of sulphur" (p. 327).

THE ALLOTROPY OF SULPHUR.

Allotropy.

The term allotropy (p. 81) was introduced by Berzelius in 1841 to describe all those cases in which an element exists in more than one form. It is thus a very general term covering many different phenomena; *e.g.*, it can be applied equally to the two solid modifications of carbon, namely, diamond and graphite, or to the two gaseous modifications of oxygen, namely, oxygen gas and ozone. In the case of sulphur, the three distinct phenomena of polymerism, isomerism, and polymorphism are all covered by this elastic term.

Polymorphism of Soluble Sulphur.

The common form of sulphur is known as SOLUBLE SULPHUR because it dissolves readily in carbon disulphide. It is capable of crystallising in four different ways and thus affords an excellent example of POLYMORPHISM. This term was introduced by Mitscherlich, in 1823, to describe those cases in which a "substance, whether simple or compound, may affect two crystalline forms." In most cases the molecules are probably identical, but are marshalled in different ways in the various crystalline forms; the differences between these forms therefore disappear when the crystalline structure is destroyed by fusion or by dissolution. The four polymorphic forms of sulphur are known as

S_I, Rhombic Sulphur.	S_{II}, Prismatic Sulphur.
S_{III}, Nacreous or Pearly Sulphur.	S_{IV}, Tabular Sulphur.

S_I, Rhombic Sulphur.

Native sulphur (Fig. 130) is found in orthorhombic crystals having three axes of twofold symmetry at right angles to one another and three planes of symmetry perpendicular to them (Fig. 131*a*). Similar crystals are obtained by evaporating a solution of sulphur in carbon disulphide.

RHOMBIC SULPHUR, as it is often called, has a density of 2·06, and is

soluble in carbon disulphide to the extent of 27 grams in 100 grams of solution at 15°. It is quite stable at atmospheric temperatures and melts at 112·8° if heated quickly; but if heated slowly it changes at 96° into prismatic sulphur, which melts several degrees higher, at 119·25°.

S_{II}, Prismatic Sulphur.

When molten sulphur is allowed to solidify in a small crucible or basin, it usually crystallises in long needles or prisms which are too slender to show the crystalline faces clearly; but when larger quantities are used, crystallisation takes place more slowly, and transparent crystals up to half an inch in diameter may be obtained.

PRISMATIC SULPHUR forms monosymmetric crystals, *i.e.*, crystals

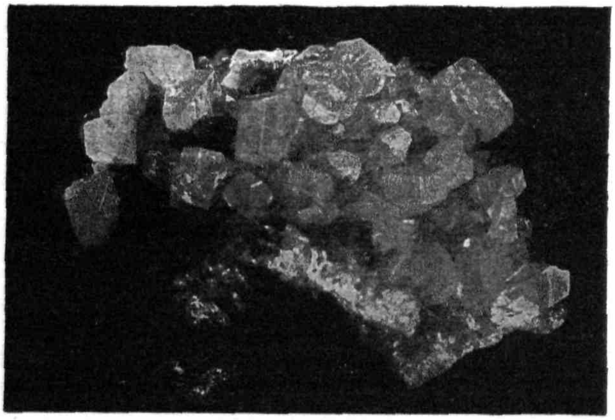


FIG. 130.—NATIVE SULPHUR (ORTHORHOMBIC).

with one axis of symmetry and one plane of symmetry at right angles to it (Fig. 131*b*). Its density is 1·98 at 0°, *i.e.*, about 5 per cent. less than the rhombic form; and it dissolves equally readily in carbon disulphide. When heated quickly it melts at 119·25°; but when the liquid is kept for a short time it undergoes partial conversion into "insoluble sulphur" (p. 321) and the freezing-point falls to 114·5°.

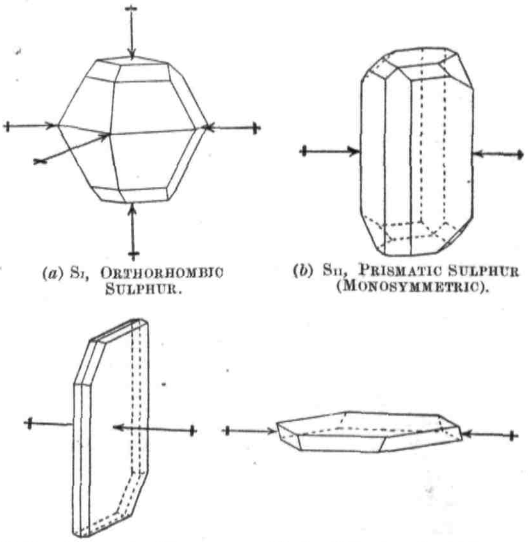
S_{III}, Nacreous Sulphur, and S_{IV}, Tabular Sulphur.

Solutions of sulphur in carbon disulphide usually desposit S_I, or rhombic sulphur, but crystals of S_{II}, or prismatic sulphur, can be obtained by adding a nucleus of this form to a saturated solution. By chilling a supersaturated solution contained in a sealed tube a third variety, S_{III}, known as NACREOUS OR PEARLY SULPHUR (Fig. 131*c*), melting at 106·8°, can sometimes be obtained; it can also be obtained

by immersing a tube of molten sulphur in boiling water and sowing it with a nucleus of nacreous sulphur crystallised from carbon disulphide as described above.

A fourth form, S_{IV}, known as TABULAR SULPHUR (Fig. 131*d*), is occasionally formed by the oxidation of solutions of ammonium sulphide in alcohol at temperatures below 14°.

Nacreous and tabular sulphur, like prismatic sulphur, are monosymmetric, with one axis of symmetry and one plane of symmetry perpendicular to it, but the angles of the three forms are quite distinct.



(*a*) S_I, ORTHORHOMBIC SULPHUR.
(*b*) S_{II}, PRISMATIC SULPHUR (MONOSYMMETRIC).
(*c*) S_{III}, NACREOUS SULPHUR (MONOSYMMETRIC).
(*d*) S_{IV}, TABULAR SULPHUR (MONOSYMMETRIC).

FIG. 131.—THE CRYSTALLINE FORMS OF SULPHUR.

Interconversion of Rhombic, Prismatic, Nacreous, and Tabular Sulphur.

Rhombic sulphur is stable up to 96°, and prismatic sulphur from 96° to the melting-point. The temperature at which this reversal of stability occurs is called the TRANSITION-POINT (compare pp. 12 and 253); it differs from a melting-point mainly in that the change of crystalline form from rhombic to prismatic sulphur, or conversely, proceeds much more slowly than the melting of ice or the freezing of water. Thus, prismatic sulphur may remain for several hours at atmospheric temperatures in a metastable condition without changing into the stable rhombic form, whereas "overcooled" water can only be preserved when special precautions are taken, *e.g.*, by suspending drops of water in oil and cooling cautiously below 0°. More remarkable is the fact that rhombic sulphur may be heated to 112·8° and melted at this temperature without changing into the prismatic form. This OVERHEATING of rhombic sulphur has no analogy in the case of ice, which is completely unstable above 0°; but substances like quartz, which form very viscous liquids, may be heated above the melting-point for a considerable time before the molecules break away from their regular marshalling and pass from the crystalline to the amorphous state. The slowness of

these changes makes it much more difficult to determine the transition-temperature of sulphur or the melting-point of quartz than the melting-point of ice or the freezing-point of water.

Rhombic and prismatic sulphur, which can be converted readily into one another, are said to be ENANTIOTROPIC (Greek, ἐναντίος, opposite; τρέπω, I turn), since they can "turn" or change in either direction. Nacreous and tabular sulphur, on the other hand, are always metastable, changing either to rhombic or to prismatic sulphur according as the temperature is below or above 96°. This change takes place only in one direction and is therefore described as MONOTROPIC. Nacreous sulphur can, however, be melted, at 106·8°, before it has had time to change into one of the other forms.

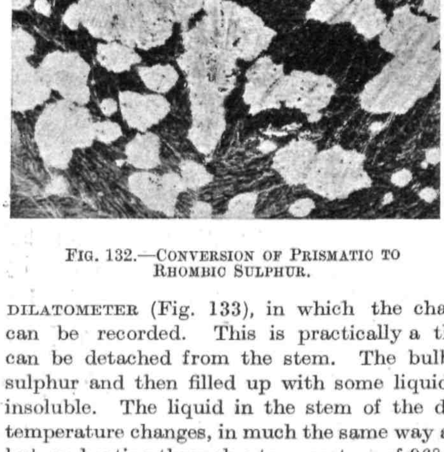


FIG. 132.—CONVERSION OF PRISMATIC TO RHOMBIC SULPHUR.

The change from prismatic to rhombic sulphur takes place most readily where nuclei of rhombic sulphur are present and therefore presents some of the features of an infectious disease. Thus, if sulphur be melted in a flat dish and allowed to solidify, the whole surface is at first transparent like amber, but on exposure to the air opaque spots appear (Fig. 132) and spread gradually until they cover the whole of the surface of the sulphur.

The transition-temperature can be determined most readily with the help of a DILATOMETER (Fig. 133), in which the changes of volume of the sulphur can be recorded. This is practically a thermometer in which the bulb can be detached from the stem. The bulb is partly filled with powdered sulphur and then filled up with some liquid in which sulphur is practically insoluble. The liquid in the stem of the dilatometer rises and falls as the temperature changes, in much the same way as the mercury in a thermometer; but, on heating through a temperature of 96°, an abrupt expansion takes place, owing to the conversion of the denser rhombic sulphur into the lighter prismatic sulphur; and, conversely, on cooling below 96°, a gradual contraction takes place, even when the temperature is kept constant, owing to the reconversion of the prismatic into the denser rhombic form.

Allotropy of Liquid Sulphur.

When sulphur is heated above the melting-point, the liquid (which is at first clear and mobile) suddenly becomes viscous at 160°. On further heating, the liquid darkens in colour and gradually becomes more mobile again as the boiling-point is approached. When the

viscous liquid is poured into water, a stringy mass of PLASTIC SULPHUR is produced, which sets to a solid in the course of a few days. The solid is a mixture of soluble sulphur (p. 317) with a form which is insoluble in carbon disulphide and is therefore known as INSOLUBLE SULPHUR.

The proportions of these two forms in the solid product depend on the temperature at which the liquid was heated, and on the speed with which it was quenched in water. Thus, by quenching quickly from the boiling-point in presence of sulphur dioxide half of the sulphur can be obtained in an insoluble form; but on cooling slowly to the melting-point the proportion of insoluble sulphur in the melt falls to 3·6 per cent. Sulphur dioxide checks the reversion of insoluble to soluble sulphur and is regarded as an anti-catalyst; hydrogen sulphide and ammonia, on the other hand, accelerate the change so much as to make it impossible to preserve the insoluble sulphur by quenching.

Molecular Weight of Soluble and Insoluble Sulphur.

The molecular weight of soluble sulphur has been determined from its effect in lowering the freezing-point of molten phosphorus and in raising the boiling-point of various solvents such as carbon disulphide, toluene, and meta-xylene. The results of these experiments indicate that the molecule of soluble sulphur must be represented by the formula S_8.

The molecular weight of insoluble sulphur has been determined from its effect in lowering the freezing-point of soluble sulphur. Prismatic sulphur, melting at 119·25°, has its freezing-point lowered in the course of a few moments to 114·5° owing to the formation in the liquid of 3·6 per cent. of insoluble sulphur. From these figures the formula S_8 has been deduced for the insoluble form.

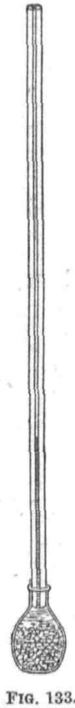


FIG. 133. DILATOMETER.

Soluble and insoluble sulphur differ widely in their properties and especially in their behaviour towards carbon disulphide, although they have the same molecular weight and are represented by the same molecular formula. They are therefore said to be ISOMERIC (Greek, ἴσος, equal, μέρος, part), a term that is used to describe substances of which the molecules are built up from the same number and kinds of atoms, but arranged in different ways in the molecule. The existence of isomerism, in this and in many other cases, affords clear evidence that the atoms are not merely jumbled together in the molecule, but are built up into some definite structure.

Sulphur Vapour.

Sulphur boils at 444·6°. Its vapour density at the boiling-points of cadmium and zinc (778° and 918°) agrees with that required by the formula S_2, but at 524° it is much higher (Dumas, 1860), corresponding

approximately with the formula S_6. More recent measurements have given values for the vapour density corresponding with the formula $S_{7\cdot0}$ at 486°, and $S_{7\cdot8}$ in measurements made under reduced pressure at 200°. These variations of vapour density can be explained by assuming that the vapour is a mixture of two kinds of molecules having the formulæ S_8 and S_2, the proportions in the equilibrium

$$S_8 \rightleftharpoons 4S_2$$

varying from one extreme to the other as the temperature is raised from 200° to 1000°. Sulphur vapour therefore affords an example of ASSOCIATION OR POLYMERISATION (p. 250), in the grouping together of the molecules of S_2 into molecules of S_8 on cooling from 1000° downwards, and of the converse process of reversible decomposition or DISSOCIATION (p. 256) of these larger molecules when the vapour is heated again to 1000°. When heated still further to 2000°, the vapour has a density corresponding with that of a monatomic molecule, S_1.

Allotropy, Polymerism, Isomerism, and Polymorphism.

From the preceding paragraphs it appears that the term allotropy as applied to sulphur covers three distinct phenomena.

(*a*) *Association and Dissociation.*—The vapour affords an illustration of reversible polymeric change, the two components of gaseous sulphur differing in the *number of atoms in the molecule.*

(*b*) *Isomerism.*—In liquid sulphur there is an equilibrium between two isomeric forms of the element which, when solid, are known as soluble and insoluble sulphur. The molecules of soluble and insoluble sulphur contain the same number of atoms, but differ in the *arrangement of the atoms in the molecule*; the actual structure is, however, not known.

(*c*) *Polymorphism.*—In the solid state the four crystalline forms of soluble sulphur afford an example of polymorphism, since all the crystals appear to be built up from identical molecules but differ in the *arrangement of the molecules in the crystal.* Of the four crystalline varieties, two, the rhombic and prismatic forms, being readily convertible into one another, are described as enantiotropic; the other two, the nacreous and tabular forms, which can only change in one direction into more stable forms, are described as monotropic.

SULPHUR AND HYDROGEN.

Hydrogen Sulphide or Sulphuretted Hydrogen, H_2S.

Sulphuretted hydrogen, the most important compound of sulphur with hydrogen, has been known for a long period as a constituent of "sulphur waters," such as those of Harrogate, and as a malodorous product of the decomposition of organic compounds, such as albumen, which contain sulphur.

Preparation of Hydrogen Sulphide.

Hydrogen sulphide is usually prepared by the action of dilute acids on ferrous sulphide, FeS, made by melting together iron and sulphur,

$$FeS + H_2SO_4 = H_2S + FeSO_4.$$

A regular stream of hydrogen sulphide may be obtained by means of the apparatus used for the preparation of hydrogen (Fig. 104, p. 222), by substituting ferrous sulphide for zinc. The gas may be collected over water already saturated with hydrogen sulphide; or it may be dried by means of fused calcium chloride or phosphoric oxide and collected over mercury, or by displacement of the air from the vessel to be filled with the gas.

The gas prepared in this way is liable to contain hydrogen and compounds of hydrogen with arsenic and carbon. It may be purified by absorbing it in a sludge of magnesium hydroxide, from which it is set free again by heating to 70°:

$$\underset{\text{Magnesium hydroxide}}{Mg(OH)_2} + 2H_2S \rightleftharpoons \underset{\text{Magnesium hydrosulphide}}{Mg(SH)_2} + 2H_2O.$$

A purer product than that obtained from ferrous sulphide can be prepared by the action of hydrochloric acid on antimony sulphide,

$$Sb_2S_3 + 6HCl = 3H_2S + 2SbCl_3.$$

or by the action of water on aluminium sulphide,

$$Al_2S_3 + 6H_2O = 3H_2S + 2Al(OH)_3.$$

Dissociation of Hydrogen Sulphide.

Hydrogen sulphide is produced when sulphur is boiled in an atmosphere of hydrogen, but this action does not provide a practical method of making the gas. The combination is exothermic,

$$S\ (\text{solid}) + H_2\ (\text{gas}) \rightleftharpoons SH_2\ (\text{gas}) + 2730\ \text{cal.},$$

although the heat liberated is only 1/25th of the heat of formation of water. Combination begins at 200°, and at 360° is sufficiently rapid to pass readily to completion. Above 400° the reverse action, indicated by the lower arrow, comes into play and (like other endothermic actions) becomes more and more important as the temperature rises. Thus the amount of hydrogen sulphide decomposed reaches

2·5 per cent.	at 700°	50 per cent.	at 1350° and
17 ,,	at 1000°	75 ,,	at 1700°.

This action may be compared with the union of sulphur dioxide with oxygen in presence of platinum (p. 334), which passes to completion at 400° but becomes less and less complete at higher temperatures.

Physical Properties of Hydrogen Sulphide.

Hydrogen sulphide is a colourless gas with an odour of rotten eggs. It may be liquefied under 17 atmospheres pressure at 18°. The liquid

has a density of 0·96, boils at — 60°, and freezes to colourless crystals melting at — 83°; the impurities may then be pumped off, leaving the solid hydrogen sulphide in a very pure state.

Hydrogen sulphide dissolves very readily in water; one volume of water dissolves 4·7 volumes of hydrogen sulphide at 0°, as compared with 4·6 volumes of chlorine, but all the gas is set free again on boiling the solution. The solution is acid towards litmus and becomes milky on exposure to air, owing to the liberation of sulphur by atmospheric oxidation.

Combustion of Hydrogen Sulphide.

Hydrogen sulphide, being composed of two inflammable constituents, burns readily in air or oxygen, but the hydrogen, being more combustible than the sulphur, is burnt first when the supply of oxygen is not sufficient to oxidise both; thus, sulphur is deposited on a cold surface held in a flame of hydrogen sulphide. The behaviour of hydrogen sulphide when sparked with and without oxygen is as follows :—

(*a*) Hydrogen sulphide is decomposed into sulphur and hydrogen without change in volume, showing that it contains its own volume of hydrogen (Dalton, 1810):

$$\underset{1\ vol.}{H_2S} = \underset{1\ vol.}{H_2} + \underset{(solid)}{S}.$$

(*b*) When exploded with half its volume of oxygen the hydrogen is burnt to water and solid sulphur is deposited (Dalton):

$$\underset{2\ vols.}{2H_2S} + \underset{1\ vol.}{O_2} = \underset{(liquid)}{2H_2O} + \underset{(solid)}{S_2}.$$

(*c*) When exploded with excess of oxygen, sulphur dioxide and water are produced:

$$\underset{2\ vols.}{2H_2S} + \underset{3\ vols.}{3O_2} = \underset{2\ vols.}{2SO_2} + \underset{(liquid)}{2H_2O}.$$

Hydrogen Sulphide as a Reducing Agent.

The heat of formation of hydrogen sulphide from its elements is only small, namely, 2730 calories for the dry gas and 7300 calories for the aqueous solution. It is therefore very ready to part with its hydrogen and to act as a reducing agent, thus :-

(*a*) Sulphur may be liberated from it by any of the ordinary oxidising agents, such as atmospheric air, chlorine, bromine, nitric acid, or chromic acid:

$$O_2 + 2H_2S = 2S + 2H_2O.$$
$$Cl_2 + H_2S = S + 2HCl.$$
$$Br_2 + H_2S = S + 2HBr,Aq.$$
$$2HNO_3 + H_2S = S + 2NO_2 + 2H_2O.$$
$$2CrO_3 + 6HCl + 3H_2S = 3S + 2CrCl_3 + 6H_2O.$$

(*b*) Hydrogen sulphide may be used instead of phosphorus to reduce iodine to hydrogen iodide:

$$H_2S + I_2 + Aq = S + 2HI,Aq.$$

It reduces sulphuric acid, which cannot therefore be used for drying the gas:

$$H_2SO_4 + H_2S = 2H_2O + SO_2 + S.$$

It also reduces sulphur dioxide to sulphur,

$$SO_2 + 2H_2S = 2H_2O + 3S;$$

in this action sulphur dioxide, which usually acts as a reducing agent, is compelled by the sulphuretted hydrogen to part with its oxygen and thus to play the part of an oxidising agent.

(*c*) In the presence of alkalies hydrogen sulphide acts as a reducing agent by absorbing oxygen instead of by liberating hydrogen. Thus, calcium sulphide in aqueous solutions is oxidised to calcium sulphite and sulphate on exposure to air,

$$2CaS + 3O_2 = \underset{\text{Calcium sulphite}}{2CaSO_3} \text{ or } CaS + 2O_2 = \underset{\text{Calcium sulphate}}{CaSO_4},$$

and moist ferrous sulphide is oxidised to ferrous sulphate,

$$FeS + 2O_2 = \underset{\text{Ferrous sulphate}}{FeSO_4}.$$

In the same way, when sulphide-ores are roasted they may either part with their sulphur or combine with oxygen:

$$2PbS + 3O_2 = 2PbO + 2SO_2$$
$$\text{or } PbS + 2O_2 = PbSO_4.$$

Hydrogen Sulphide as an Acid.

Hydrogen sulphide imparts an acid reaction to water and in many of its chemical properties behaves as a weak dibasic acid. Thus, it is absorbed by caustic potash with the production of potassium sulphide, K_2S, and potassium hydrogen sulphide, KSH:

$$2KOH + H_2S = K_2S + 2H_2O.$$
$$KOH + H_2S = KSH + H_2O.$$

The displacement of hydrogen sulphide from ferrous sulphide by acids may be compared with the preparation of hydrogen chloride from salt by the action of sulphuric acid.

Hydrogen Sulphide in Analysis.

(*a*) The majority of the metals form sulphides which are insoluble in water. Exceptions are

(i) The metals of the alkalies and alkaline earths which form soluble sulphides;

(ii) Aluminium, chromium, and ferric iron, the sulphides of which are not stable in presence of water.

The addition of a soluble sulphide to a soluble salt of a metal, such as

copper or zinc, will therefore usually precipitate the insoluble sulphide of the metal:

$$CuCl_2 + Na_2S = CuS + 2NaCl.$$
$$ZnCl_2 + Na_2S = ZnS + 2NaCl.$$

(*b*) These insoluble sulphides may be subdivided according to their behaviour towards acids and alkalies. Thus, if hydrogen sulphide be used instead of sodium sulphide, the precipitation of a soluble sulphide will involve the displacement of a strong acid by a weak one, *e.g.*,

$$CuCl_2 + H_2S = CuS + 2HCl.$$

There are then two opposing tendencies at work, namely,

(i) The tendency for the insoluble sulphide to be precipitated;
(ii) The tendency of a strong acid to displace a weak one.

In practice it is found that under these conditions some metals are precipitated as sulphides whilst others remain in solution; thus, copper sulphide is precipitated by sulphuretted hydrogen even in presence of acids, whilst zinc sulphide dissolves in acids and can only be precipitated in neutral or alkaline solutions:

$$CuCl_2 + H_2S \longrightarrow CuS + 2HCl.$$
$$ZnCl_2 + H_2S \longleftarrow ZnS + 2HCl.$$

In the case of cadmium, the action is reversible,

$$CdCl_2 + H_2S \rightleftharpoons CdS + 2HCl,$$

proceeding in one direction or the other according to the proportions of acid and water in the solution. By taking advantage of this difference the sulphides which are insoluble in water may be divided into two groups according as they can or cannot be precipitated in presence of mineral acids.

These differences are interpreted in terms of the theory of electrolytic dissociation by saying that copper sulphide has a smaller "solubility product" (p. 203) than zinc sulphide, and that the concentration of sulphide-ions is higher in a solution of sodium sulphide than in a solution of hydrogen sulphide.

(*c*) A further distinction is found in the fact that the sulphides of the less well-defined metals unite with alkali-sulphides to form soluble SULPHO-SALTS (Berzelius, 1826) which are analogous in many ways to the ordinary oxy-salts. Thus, the sulphides of arsenic, antimony, and one of the sulphides of tin * are soluble in sodium sulphide.

$$As_2S_3 + 3Na_2S = \underset{\text{Sodium sulpharsenite}}{2Na_3AsS_3}.$$

$$Sb_2S_3 + 3Na_2S = \underset{\text{Sodium sulphantimonite}}{2Na_3SbS_3}.$$

$$SnS_2 + Na_2S = \underset{\text{Sodium sulphostannate}}{Na_2SnS_3}.$$

* Stannous sulphide, SnS, unlike stannic sulphide, SnS_2, is only soluble in sodium sulphide in the presence of air or sulphur.

Lead, copper, mercury, bismuth, and cadmium do not form soluble sulpho-salts, and their sulphides are therefore not dissolved by sodium sulphide. In this way, therefore, the sulphides which do not dissolve in acids can be further divided according to their solubility or insolubility in solutions of sodium sulphide or ammonium sulphide. These successive subdivisions of the sulphides are the principal feature of the common system of qualitative analysis.

Liver of Sulphur.

Hydrogen sulphide and sulphur dioxide interact, when moist, according to the equation

$$2H_2S + SO_2 = 2H_2O + 3S,$$

to form sulphur and water; but as the sulphide and oxide are both acids, this action can be reversed by the addition of alkalies. These dissolve sulphur, forming for instance potassium sulphide and potassium sulphite as shown in the equation

$$3S + 6KOH = \underset{\text{Potassium sulphide}}{2K_2S} + \underset{\text{Potassium sulphite}}{K_2SO_3} + 3H_2O.$$

On the addition of acids the sulphur is reprecipitated,

$$2K_2S + K_2SO_3 + 6HCl = 6KCl + 3H_2O + 3S.$$

The sulphide formed in this action may combine with a further quantity of sulphur to form POLYSULPHIDES, such as K_2S_2 and K_2S_4, whilst the sulphite may combine with sulphur to form a THIOSULPHATE, *e.g.*, $K_2S_2O_3$. The formation of these compounds increases the amount of sulphur which is dissolved by the alkali and reprecipitated by the addition of acids. The mixture of polysulphides and thiosulphate obtained as a liver-brown mass by fusing potassium carbonate with sulphur, *e.g.*,

$$3K_2CO_3 + 6S = \underset{\text{Potassium disulphide}}{2K_2S_2} + \underset{\text{Potassium thiosulphate}}{K_2S_2O_3} + 3CO_2,$$

is used in medicine under the name of LIVER OF SULPHUR, and the sulphur which is reprecipitated by acids is known as MILK OF SULPHUR.

Hydrogen Persulphides.

Corresponding with the alkali-polysulphides, a mixture of hydrogen polysulphides is formed as a yellow oil when a solution of sulphur in aqueous sodium sulphide is added to ice-cold dilute hydrochloric acid. By the fractional distillation of the crude oil **hydrogen disulphide,** H_2S_2, is obtained as a yellow liquid, boiling at 74°. It is readily decomposed by water and alkalies, but combines with aldehydes (p. 451) to form crystalline compounds of the type $(C_2H_4O)_2,H_2S_2$. **Hydrogen trisulphide,** H_2S_3, separated from the higher-boiling fractions of the same liquid, is a yellow oil, boiling at 69° under a pressure of 2 mm.; it solidifies to

colourless crystals melting at — 53°. It decomposes in sunlight, giving sulphuretted hydrogen and rhombic sulphur,

$$H_2S_3 = H_2S + 2S;$$

it is also decomposed by water and alkalies, and like the disulphide forms white crystalline compounds with aldehydes, *e.g.*, $(C_2H_4O)_2,H_2S_3$.

SULPHUR AND OXYGEN.

Oxides and Acids of Sulphur.

Sulphur forms a large number of oxides and oxy-acids. The most important oxides are

Sulphur dioxide, SO_2 (or sulphurous anhydride)

Sulphur trioxide, SO_3 (or sulphuric anhydride).

The corresponding acids are

Sulphurous acid, H_2SO_3 forming a series of SULPHITES

Sulphuric acid, H_2SO_4 forming a series of SULPHATES.

Sulphurous and sulphuric acids, being dibasic, can form two series of salts, *e.g.*,

Sodium sulphite, Na_2SO_3
Sodium hydrogen sulphite, or sodium bisulphite, $NaHSO_3$

Sodium sulphate, Na_2SO_4
Sodium hydrogen sulphate or sodium bisulphate, $NaHSO_4$.

Salts derived from the acid salts by loss of water and containing two atoms of sulphur are known as

Sodium metabisulphite, $Na_2S_2O_5$. **Sodium pyrosulphate,** $Na_2S_2O_7$.

The crystalline acid, $H_2S_2O_7$, from which the latter salt is derived is known as **pyrosulphuric acid.**

In accordance with the general system of naming acids and salts, the terms HYPOSULPHUROUS ACID and HYPOSULPHITES should be reserved for compounds containing less oxygen than sulphurous acid and the sulphites, *e.g.*, for compounds such as H_2SO_2, Na_2SO_2, and $CaSO_2$; unfortunately these terms have been used to describe compounds containing more sulphur, instead of less oxygen, namely, THIOSULPHURIC ACID, $H_2S_2O_3$ and the THIOSULPHATES, such as $Na_2S_2O_3$ and CaS_2O_3 (p. 579), or with equally little justification to salts of the type $Na_2S_2O_4$, ZnS_2O_4, etc. (p. 332).

In a similar manner, the general system of nomenclature reserves the terms PERSULPHURIC ACID and PERSULPHATES for compounds richer in oxygen than sulphuric acid and the sulphates. Two acids of this class are known, namely,

Caro's persulphuric acid, H_2SO_5;
Marshall's persulphuric acid, $H_2S_2O_8$.

The former is a monobasic acid forming only salts such as $NaHSO_5$;

the latter is a dibasic acid forming salts such as $Na_2S_2O_8$ (p. 581). The two acids are commonly distinguished as

per*mono*sulphuric acid, H_2SO_5 (*i.e.*, $SO_3 + H_2O_2$),
per*di*sulphuric acid, $H_2S_2O_8$ (*i.e.*, $2SO_3 + H_2O_2$);

this distinction being based upon the empirical formulæ (shown in brackets) which represent these acids as compounds of hydrogen peroxide with one and with two molecules of sulphuric anhydride.

The anhydride of per*di*sulphuric acid is known as **disulphur heptoxide,** S_2O_7. A fourth oxide of sulphur, prepared from sulphur trioxide and sulphur, is known as **sulphur sesquioxide,** or **disulphur trioxide,** S_2O_3.

Preparation of Sulphur Dioxide, SO_2.

(*a*) *By burning Sulphur.*—Sulphur burns in air or oxygen without producing any marked change of volume.

$$\underset{}{S} + \underset{1\ vol.}{O_2} = \underset{1\ vol.}{SO_2}.$$

The principal product, sulphur dioxide, is a colourless gas containing its own volume of oxygen. About 7 per cent. of the oxygen is, however, converted into sulphur trioxide when sulphur is burnt in air and about 2·5 per cent. when pure oxygen is used; under a pressure of 40 atmospheres of oxygen, about 50 per cent. of the sulphur is converted into the trioxide. The particles of the solid trioxide have the effect of making the gas appear cloudy.

Commercial sulphur dioxide is prepared by dissolving the crude gas in cold water, driving it out again by heat, drying with sulphuric acid, and then compressing to a liquid.

(*b*) *By burning Sulphides.*—Sulphur dioxide is prepared commercially (*e.g.*, in the manufacture of sulphuric acid) by burning iron pyrites,

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

The crude gas contains arsenious oxide, As_4O_6, sulphur trioxide, SO_3, and dust as impurities. It may be purified by passing it through settling chambers, coke filters, and coke towers with sulphuric acid flowing down them (compare Fig. 134, p. 335).

Crude sulphur dioxide is also prepared by roasting other mineral sulphides, *e.g.*, ZnS, and by burning "spent iron oxide" from the gas-works, which contains ferrous sulphide, FeS, and free sulphur.

(*c*) *By reducing Sulphuric Acid.*—Gaseous sulphur dioxide was first isolated in 1774 by Priestley, who prepared the gas by the action of olive oil, and then of charcoal and mercury on concentrated oil of vitriol; in the two former cases carbon dioxide is also produced.

$$C + 2H_2SO_4 = 2SO_2 + CO_2 + 2H_2O.$$
$$Hg + 2H_2SO_4 = SO_2 + 2H_2O + HgSO_4.$$

Sulphur dioxide can also be prepared by the action of copper on concentrated sulphuric acid,

$$Cu + 2H_2SO_4 = SO_2 + 2H_2O + CuSO_4;$$

the action is, however, a complex one, in which considerable quantities of copper sulphide are also produced; it is therefore only used as a laboratory method for preparing small quantities of the gas.

Physical Properties of Sulphur Dioxide.

Sulphur dioxide is a colourless gas with a pungent odour, and is just twice as dense as oxygen. It can be liquefied under a vapour pressure of 3 atmospheres at 18°. The liquid boils at — 10° under a pressure of 760 mm., has a density of 1·46 at the boiling-point, and freezes to a solid melting at — 73°. Liquid sulphur dioxide is sold commercially in glass syphons closed by means of a gun-metal valve. When a syphon of sulphur dioxide is inverted so as to deliver liquid instead of gas, the escaping liquid cools to the normal boiling-point of — 10° and can be used as a cooling agent; its temperature may be reduced still further by blowing air through it.

Liquid sulphur dioxide dissolves a number of metallic salts, *e.g.*, potassium iodide, KI, and is one of the few solvents which give solutions that are capable of conducting an electric current (compare p. 250). When solutions of salts in sulphur dioxide are cooled, various compounds of sulphur dioxide with the solute crystallise out.

Sulphur Dioxide and Water.

Water dissolves 80 volumes of sulphur dioxide at 0° (as compared with about 5 volumes of H_2S or Cl_2), but the greater part of the gas escapes on exposure to the air and the whole of it can be driven off by boiling the solution. At temperatures above 12°, liquid sulphur dioxide (under pressure) and water form two layers like ether and water; the upper aqueous layer contains 23·7 per cent. of SO_2, whilst the lower layer, containing 98·6 per cent. of SO_2, is almost pure sulphur dioxide; liquid sulphur dioxide also forms two layers with sulphuric acid, although it mixes freely in all proportions with sulphur trioxide. On cooling, a **hydrate**, $SO_2,7H_2O$ or $H_2SO_3,6H_2O$, crystallises out from the aqueous solution. The solution is strongly acid and probably contains SULPHUROUS ACID, H_2SO_3, although this acid has not been isolated.

Chemical Properties of Sulphur Dioxide.

(*a*) *Acid Properties.*—Sulphur dioxide in aqueous solutions has all the properties of a weak dibasic acid. It combines with alkalies and with basic oxides to form neutral SULPHITES and acid BISULPHITES, in

addition to METABISULPHITES derived from the hypothetical acid $H_2S_2O_5$.

$$2NaOH + SO_2 = \underset{\text{Sodium sulphite}}{Na_2SO_3} + H_2O.$$

$$2NaOH + 2SO_2 = \underset{\text{Sodium bisulphite}}{2NaHSO_3} = \underset{\text{Sodium metabisulphite}}{Na_2S_2O_5} + H_2O.$$

$$\underset{\text{Slaked lime}}{Ca(OH)_2} + SO_2 = \underset{\text{Calcium sulphite}}{CaSO_3} + H_2O.$$

Calcium sulphite, prepared by the action of sulphur dioxide on milk of lime, is used very largely to disintegrate wood fibre in the manufacture of paper pulp.

(*b*) *Sulphur Dioxide as a Reducing Agent.*—Sulphur dioxide gas has very little tendency to combine directly with oxygen, and does not fume on exposure to air. In the presence of water or of alkalies it oxidises more readily, since water and alkalies have much more affinity for sulphur trioxide than for the dioxide. This is shown very clearly by the thermo-chemical equations for the three oxidations :

$$SO_2\,(gas) + \tfrac{1}{2}O_2 = SO_3\,(gas) + 32{,}160 \text{ calories.}$$
$$H_2SO_3,aq + \tfrac{1}{2}O_2 = H_2SO_4,aq + 63{,}630 \text{ calories.}$$
$$K_2SO_3,aq + \tfrac{1}{2}O_2 = K_2SO_4,aq + 63{,}280 \text{ calories.}$$

The ready oxidation of sulphur dioxide in solution may be shown by dissolving the gas in air-free water and adding barium chloride ; as barium sulphite is soluble in acids, no change is noticed until oxidation to sulphuric acid has taken place, when barium sulphate is at once precipitated, *e.g.*, on exposure to air,

$$2SO_2 + O_2 + 2H_2O + 2BaCl_2 = 2BaSO_4 + 4HCl.$$

More rapid oxidation takes place on the addition of hydrogen peroxide, H_2O_2, chlorine water, ferric chloride, $FeCl_3$, potassium chromate, K_2CrO_4, or potassium permanganate, $KMnO_4$.

$$H_2O_2 + H_2SO_3 = H_2O + H_2SO_4.$$
$$Cl_2 + H_2O + H_2SO_3 = 2HCl + H_2SO_4.$$
$$\underset{\text{Ferric chloride}}{2FeCl_3} + H_2O + H_2SO_3 = \underset{\text{Ferrous chloride}}{2FeCl_2} + 2HCl + H_2SO_4.$$
$$\underset{\text{Potassium dichromate}}{K_2Cr_2O_7} + H_2SO_4 + 3H_2SO_3 = \underset{\text{Potassium sulphate}}{K_2SO_4} + \underset{\text{Chromium sulphate}}{Cr_2(SO_4)_3} + 4H_2O.$$
$$\underset{\text{Potassium permanganate}}{2KMnO_4} + 5H_2SO_3 = \underset{\text{Potassium sulphate}}{K_2SO_4} + \underset{\text{Manganese sulphate}}{2MnSO_4} + 2H_2SO_4 + 3H_2O.$$

(*c*) *Bleaching Action of Sulphur Dioxide.*—Sulphur dioxide reduces many coloured compounds to colourless derivatives and is frequently

used as a bleaching agent for substances such as straw and sponge, which are injured by bleaching powder; the oxidising action of air and light restores the original yellow colour to straw, but it may be rendered white again by washing it with a solution of sulphur dioxide. Sulphur dioxide is also used as a disinfectant.

(*d*) *Oxidising Action of Sulphur Dioxide.*—Although sulphur dioxide usually acts as a reducing agent, it can sometimes be made to part with its oxygen and thus to assume the *rôle* of an oxidising agent. This is notably the case with sulphuretted hydrogen, which interacts with sulphur dioxide according to the equation

$$SO_2 + 2H_2S = 2H_2O + 3S.$$

Ferrous chloride can also be oxidised to ferric chloride by the action of sulphur dioxide.

$$4FeCl_2 + 4HCl + SO_2 = 4FeCl_3 + 2H_2O + S.$$

(*e*) *Additive Compounds of Sulphur Dioxide.*—Although most of the combining power of sulphur is satisfied by combination with two atoms of oxygen, a certain amount of affinity remains available for the direct combination of sulphur dioxide with other substances. Thus, as shown under (*c*) above, it combines with *water* to form sulphurous acid, H_2SO_3, and with *metallic oxides* to form sulphites. Sulphur dioxide combines directly with certain *metals* to form HYDROSULPHITES, *e.g.*,

$$Zn + 2SO_2 = \underset{\text{Zinc hydrosulphite}}{ZnS_2O_4},$$

derived from the acid $H_2S_2O_4$; these were at one time thought to be real hyposulphites derived from the acid H_2SO_2, *e.g.*, $ZnSO_2$, but have been proved to belong to the S_2 and not to the S_1 series. It also combines, with incandescence, with some solid *metallic peroxides* with the formation of SULPHATES,

$$PbO_2 + SO_2 = PbSO_4.$$
$$Na_2O_2 + SO_2 = Na_2SO_4.$$

In the case of manganese dioxide it forms both a sulphate and a DITHIONATE derived from the acid $H_2S_2O_6$.

$$MnO_2 + SO_2 = \underset{\text{Manganese sulphate}}{MnSO_4};$$
$$MnO_2 + 2SO_2 = \underset{\text{Manganese dithionate}}{MnS_2O_6}.$$

Sulphur dioxide combines with *oxygen* in the presence of platinum black to form sulphur trioxide, SO_3, and with *chlorine* in presence of camphor to form sulphuryl chloride, SO_2Cl_2 (see below), whilst the sulphites

derived from it combine both with *oxygen* to form sulphates and with *sulphur* to form thiosulphates.

$$Na_2SO_3 + \tfrac{1}{2}O_2 = \underset{\text{Sodium sulphate}}{Na_2SO_4}.$$

$$Na_2SO_3 + S = \underset{\text{Sodium thiosulphate}}{Na_2S_2O_3}.$$

(*f*) *Sulphuryl Chloride and Thionyl Chloride.*—(i) Sulphur dioxide combines with chlorine in bright sunlight, or in the presence of acetic acid or of camphor, to form **sulphuryl chloride,** SO_2Cl_2, by the direct *addition* of two atoms of chlorine:

$$\underset{1\ vol.}{SO_2} + \underset{1\ vol.}{Cl_2} = \underset{\text{(liquid)}}{SO_2Cl_2}.$$

Sulphuryl chloride is a colourless, fuming liquid, of density 1·71 and boiling at 70°, which is readily decomposed by water with the formation of sulphuric and hydrochloric acids.

$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl.$$

(ii) The action of phosphorus pentachloride, on the other hand, results in the formation of **thionyl chloride,** $SOCl_2$, by the *substitution* of two atoms of chlorine for one of oxygen, *e.g.*,

$$SO_2 + PCl_5 = \underset{\text{Thionyl chloride}}{SOCl_2} + \underset{\text{Phosphorus oxychloride}}{POCl_3}.$$

Thionyl chloride can also be prepared by the action of sulphur trioxide on the liquid (perhaps a mixture of S_2Cl_2 and SCl_4) which is commonly known as sulphur dichloride, SCl_2.

$$SO_3 + SCl_2 = SOCl_2 + SO_2.$$

Thionyl chloride resembles sulphuryl chloride somewhat closely. It is a colourless, fuming liquid having a density of 1·68 at 0° and boils at 79°, as compared with 1·71 and 70° for SO_2Cl_2. It is decomposed by water, forming sulphurous acid, H_2SO_3, and hydrochloric acid, and with ammonia gives **thionamide,** $SO(NH_2)_2$, and ammonium chloride.

$$SOCl_2 + 2H_2O = H_2SO_3 + 2HCl.$$

$$SOCl_2 + 4NH_3 = \underset{\text{Thionamide}}{SO(NH_2)_2} + \underset{\text{Ammonium chloride}}{2NH_4Cl}.$$

Preparation of Sulphur Trioxide by the Contact Process.

(*a*) *Oxidation of Sulphur Dioxide in Presence of Platinum.*—Sulphur dioxide and oxygen unite together readily in the presence of finely-divided platinum, *e.g.*, platinum black, or platinised asbestos, or platinum deposited on anhydrous magnesium sulphate. This method of preparing sulphur trioxide is known as the CONTACT PROCESS.

A mixture of sulphur dioxide and oxygen from which sulphur

trioxide could be manufactured was formerly prepared by "cracking" oil of vitriol by dropping it into a red-hot retort,

$$2H_2SO_4 = 2H_2O + 2SO_2 + O_2.$$

The sulphur dioxide and oxygen were dried with oil of vitriol and were united again by contact with platinum,

$$2SO_2 + O_2 = 2SO_3.$$

The sulphur trioxide was condensed by cooling, or absorbed in oil of vitriol in order to convert it into the fuming acid.

(*b*) *Purification of Gases.*—Attempts to use this method to prepare sulphur trioxide from the crude gas obtained by burning iron pyrites or sulphur in air failed, because the platinum soon lost its catalytic power. The loss of activity was traced to "poisoning" of the catalyst in part by "acid mist" from the pyrites burners, but more especially by arsenious oxide, As_4O_6; when the gas is filtered and washed until it is perfectly clear and free from fog, the activity of the catalyst can be maintained over a period of some years, and the process may then be worked industrially on a large scale for the preparation of fuming acid and even of ordinary concentrated sulphuric acid.

(*c*) *Composition of Mixture.*—The combination of sulphur dioxide and oxygen is a balanced action, as shown by the equation

$$2SO_2 + O_2 \rightleftharpoons 2SO_3;$$

the percentage of sulphur dioxide converted into sulphur trioxide therefore increases with the quantity of oxygen present. In the commercial process the gas supplied to the converter contains about 7 per cent. of SO_2, 10 per cent. of O_2, and 83 per cent. of N_2, so that three times as much oxygen is present as would be required to convert the whole of the sulphur dioxide to sulphur trioxide.

(*d*) *Temperature of Conversion.*—The oxidation of sulphur dioxide to sulphur trioxide is exothermic,

$$SO_2 \text{ (gas)} + \tfrac{1}{2}O_2 \rightleftharpoons SO_3 \text{ (liquid)} + 32{,}160 \text{ calories};$$

as in the case of other exothermic actions, therefore, the reverse change, leading to the decomposition of the trioxide, becomes more and more important as the temperature rises. Thus, for the composition 7 per cent. SO_2, 10 per cent. O_2, 83 per cent. N_2, the maximum conversion at different temperatures is as follows :—

At 434°, 99 per cent. SO_3;
At 550°, 85 per cent. SO_3;
At 640°, 60 per cent. SO_3.

It is for this reason that platinum, which will bring about a rapid oxidation at 420°, is so much more effective as a catalyst than ferric oxide, which becomes an active catalyst only at 600°, *i.e.*, at a temperature at which oxidation stops when two-thirds of the dioxide has been converted into trioxide.

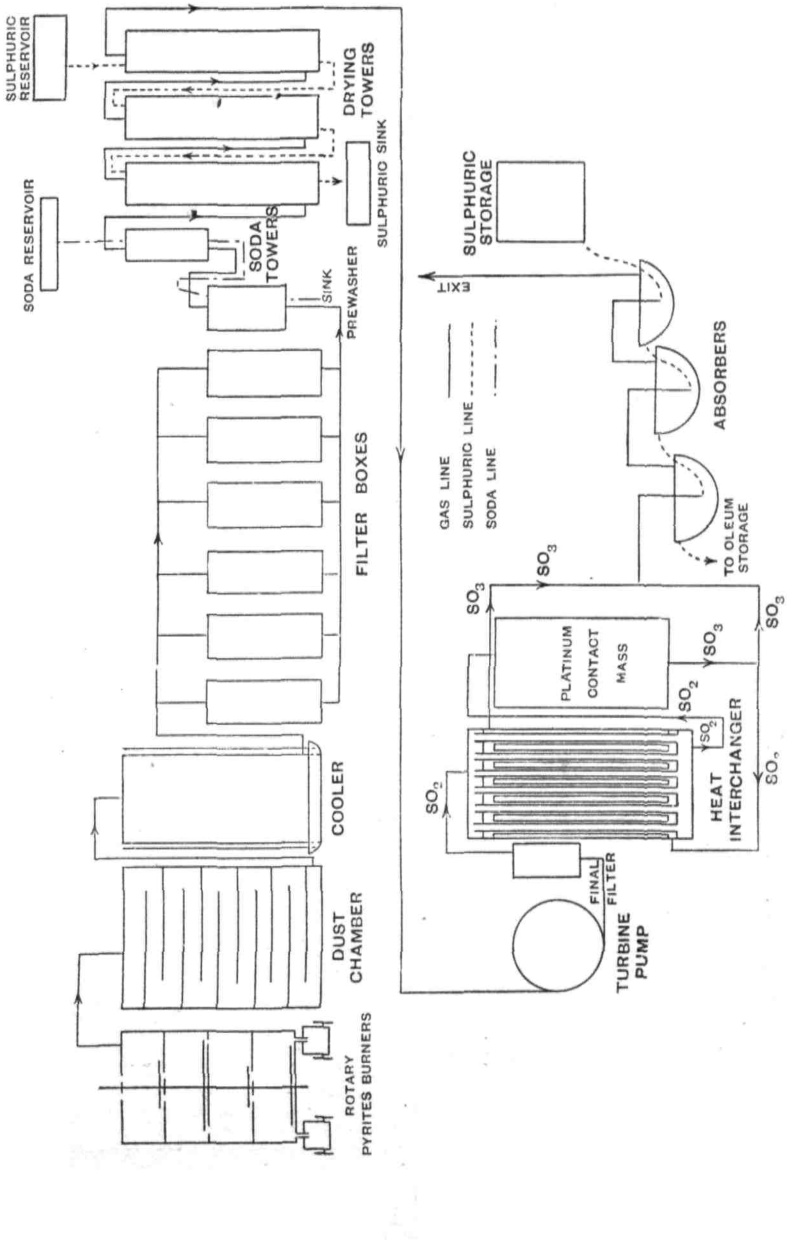


FIG. 134.—DIAGRAMMATIC REPRESENTATION OF CONTACT-PROCESS FOR MANUFACTURE OF SULPHUR TRIOXIDE.

In order to secure rapid combination of sulphur dioxide and oxygen it is necessary to raise the temperature of the platinum to about 400°, although the conversion can be started with gas at about 300°. In practice the gas can be preheated sufficiently by making use of the heat set free in the burning of the pyrites or sulphur to the dioxide,

$$S + O_2 = SO_2 + 70{,}000 \text{ calories},$$

and in the oxidation of the dioxide to trioxide,

$$SO_2 + \tfrac{1}{2}O_2 = SO_3 + 32{,}160 \text{ calories}.$$

This heat is utilised (compare Fig. 134) by heating the cold clean gases,

(i) in a "heat-exchanger" warmed by the gases from the converter,
(ii) in a "heater-cooler" heated by the hot gases from the burners,* and
(iii) by an exchange of heat in the converter itself.

In order to secure complete conversion it is necessary to take care that the heat liberated during the oxidation does not raise the temperature in the converter above the point at which practically complete oxidation can be secured. Arrangements are therefore made whereby the gases which have been heated above 420° by oxidation in the converter are brought down again to this temperature by the gases entering the converter at 300° from the "heat-exchanger" and "heater-cooler" referred to above. These warm gases are made to circulate round the outside of the converter before they pass downwards through the catalyst. In this way it is possible to ensure that the final stage of the conversion takes place at the optimum temperature of 420°, although in the initial stages of oxidation the temperature may rise to 550°.

(*e*) *Character of the Product.*—The sulphur trioxide produced in this way is mixed with large quantities of nitrogen and in spite of its hygroscopic nature is not easily absorbed by water. In practice therefore the sulphur trioxide is absorbed by oil of vitriol containing 97–99 per cent. of sulphuric acid, and if the product is too strong, it is diluted by the addition of water or dilute acid.

The main value of the contact process is in the production of the highly concentrated or fuming acid known commercially as OLEUM. Sulphuric acid made in this way has, however, the advantage of being specially pure, and in particular is practically free from arsenic; it is therefore suitable for filling lead accumulators and for the manufacture of glucose from starch, where freedom from arsenic is essential.

Physical Properties of Sulphur Trioxide.

Sulphur trioxide exists in two forms. The α-form melts at 17° and boils at 45° under the normal pressure; the density of the liquid is 1·923 at 20°. When the α-form is left in contact with moist air it changes into the β-form, an asbestos-like solid, which volatilises without melting at 50°, yielding the ordinary vapour. It has been suggested that the β-form has the formula S_2O_6, but the molecular weight of both forms, determined cryoscopically with phosphoryl chloride, $POCl_3$, as solvent, corresponds with the formula SO_3. The α-form is chemically much more active than the β-form.

* Not shown in Fig. 134.

Sulphur Trioxide and Water.

(*a*) *Formation of Hydrates.*—Sulphur trioxide unites with water to form a series of crystalline hydrates.

TABLE 41.—HYDRATES OF SULPHUR TRIOXIDE.

Name.	*Composition.*	*Melting-point.*
Pyrosulphuric acid,	$2SO_3,H_2O$ or $H_2S_2O_7$	36°
Sulphuric acid,	SO_3,H_2O or H_2SO_4	10·4°
Sulphuric acid monohydrate,*	$SO_3,2H_2O$ or H_2SO_4,H_2O	8·5°
Sulphuric acid dihydrate,	$SO_3,3H_2O$ or $H_2SO_4,2H_2O$	−39°
Sulphuric acid tetrahydrate,	$SO_3,5H_2O$ or $H_2SO_4,4H_2O$	−25°

The temperatures at which these hydrates begin to crystallise from solutions of different compositions are shown in Fig. 135.

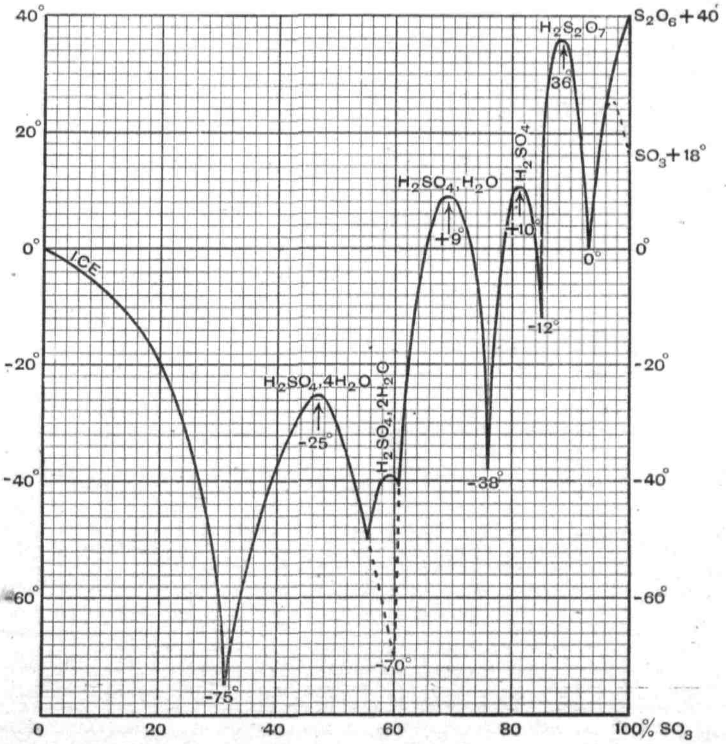


FIG. 135.—FREEZING-POINT DIAGRAM FOR SULPHUR TRIOXIDE AND WATER.

* The name "monohydrate" is, however, still applied commercially to SO_3,H_2O, *i.e.*, to anhydrous sulphuric acid, in accordance with the old nomenclature in which the oxide SO_3 was described as sulphuric acid.

With the exception of **pyrosulphuric acid,** $H_2S_2O_7$, and **sulphuric acid,** H_2SO_4, it is not easy to crystallise out these hydrates unless a crystal is already available with which to inoculate the liquid. The hydrate, $H_2SO_4,2H_2O$, is especially difficult to prepare and in any case melts as soon as the temperature rises above $-39°$.

The combination of sulphur trioxide with water is an exothermic action, accompanied by the liberation of much heat:

$$SO_3 \text{ (liq.)} + H_2O \text{ (liq.)} = H_2SO_4 \text{ (liq.)} + 21{,}300 \text{ cal.}$$
$$H_2SO_4 \text{ (liq.)} + Aq = H_2SO_4, Aq + 18{,}000 \text{ cal. (about)}$$

Thus 21,300 calories are liberated in the conversion of sulphur trioxide to sulphuric acid and a further 18,000 calories when the sulphuric acid is diluted with a large bulk of water, a total of over 39,000 calories, as compared with 68,360 calories for the heat of formation of water.

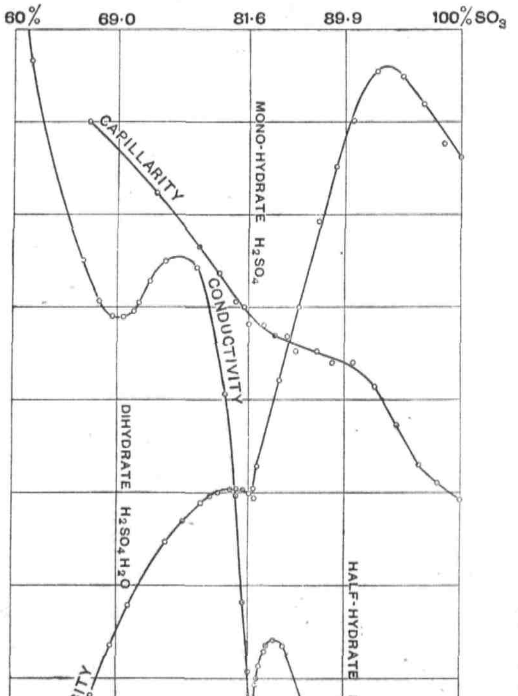


FIG. 136.—PHYSICAL PROPERTIES OF SULPHUR TRIOXIDE AND ITS HYDRATES.

(*b*) *Dissociation of Hydrates on Fusion.*—When these hydrates are melted, partial dissociation immediately takes place; for instance, crystalline sulphuric acid, H_2SO_4, probably breaks down partially on fusion into fuming sulphuric acid on the one hand and more watery hydrates on the other, *e.g.*,

$$3H_2SO_4 \rightleftharpoons H_2S_2O_7 + H_2SO_4,H_2O.$$

The existence of the compound, H_2SO_4, in the liquid state is, however, shown clearly by sharp kinks at 81·6 per cent. of SO_3 (or 100 per cent. of H_2SO_4) in the curves representing the density, capillarity, and electrical conductivity of mixtures of sulphur trioxide and water (Fig. 136). In the same way, the existence of the half-hydrate, $2SO_3,H_2O$ or $H_2S_2O_7$, known as pyro-

sulphuric acid, in the liquid state, is indicated on the capillarity curve, whilst the curve of electrical conductivity reveals the presence of the hydrate, H_2SO_4,H_2O, by passing through a well-defined minimum at this point.

(*c*) *Dissociation of Hydrates on Distillation.*—As the temperature is raised, dissociation of the hydrates increases, and at high temperatures sulphuric acid of the composition H_2SO_4 probably contains both sulphur trioxide and free water. When distilled, anhydrous sulphuric acid,

$$H_2SO_4 \rightleftharpoons SO_3 + H_2O,$$

loses sulphur trioxide until the concentration falls to 98·33 per cent. of H_2SO_4, when a mixture of this composition distils at a constant temperature of 330°. Conversely, when dilute sulphuric acid is heated, water distils until the boiling-point has risen to 330° and the concentration to 98·33 per cent. H_2SO_4, after which the mixture again distils at a constant temperature. This mixture of constant boiling-point is not a chemical compound and cannot be represented by a single formula : it may be regarded, however, as a mixture of the compound, H_2SO_4, with the products of its own dissociation (compare hydrochloric acid, p. 284).

It will be seen that the behaviour of sulphur trioxide is in complete contrast with that of the dioxide, which can be removed completely from its solutions by boiling.

Additive Compounds of Sulphur Trioxide.

In addition to combining with *water* to form sulphuric acid and other hydrates, and with *metallic oxides* such as magnesia (Fig. 105, p. 239) to form salts, sulphur trioxide will unite with *hydrogen peroxide* to form persulphuric acids (p. 348), with *oxygen* under the influence of the electric discharge to form the heptoxide S_2O_7 (p. 347), with *sulphur* to form the sesquioxide S_2O_3, and with *hydrogen chloride* to form chlorosulphonic acid, SO_3HCl. It also combines with *sulphuryl chloride*, SO_2Cl_2, to form pyrosulphuryl chloride, $S_2O_5Cl_2$, just as it combines with *sulphuric acid*, H_2SO_4, to form pyrosulphuric acid, $H_2S_2O_7$.

Disulphur Trioxide or **Sulphur Sesquioxide,** S_2O_3, is formed when flowers of sulphur are added to sulphur trioxide kept just above its melting-point. As each small portion of sulphur is added, drops of a deep blue colour sink to the bottom of the liquid trioxide and solidify. After all the sulphur has been added, the trioxide is poured off and the sesquioxide is left as a bluish-green, crystalline mass, which decomposes at the ordinary temperature; giving off sulphur dioxide and leaving a residue of sulphur. It is decomposed at once by water, giving thiosulphuric, sulphuric, and sulphurous acids.

$$3S_2O_3 + 4H_2O = \underset{\text{Thiosulphuric acid}}{2H_2S_2O_3} + \underset{\text{Sulphuric acid}}{H_2SO_4} + \underset{\text{Sulphurous acid}}{H_2SO_3}.$$

Sulphur sesquioxide, although insoluble in pure sulphur trioxide, is

soluble in fuming sulphuric acid, giving a blue solution which gradually turns green and then brown.

Chlorosulphonic acid, $ClSO_3H$, is prepared by the direct addition of hydrogen chloride to sulphur trioxide, or by distilling a mixture of fuming sulphuric acid which has been saturated with hydrogen chloride:

$$SO_3 + HCl = ClSO_3H.$$

Chlorosulphonic acid is a colourless fuming liquid boiling at 155° and has a density of 1·78 at 0°. It decomposes at 200° into sulphuryl chloride (p. 333) and sulphuric acid according to the equation

$$2ClSO_3H = SO_2Cl_2 + H_2SO_4,$$

and is decomposed by water, yielding sulphuric and hydrochloric acids:

$$ClSO_3H + H_2O = HCl + H_2SO_4.$$

Pyrosulphuryl chloride, $S_2O_5Cl_2$, is formed by the direct combination of sulphur trioxide and sulphuryl chloride,

$$SO_3 + SO_2Cl_2 = S_2O_5Cl_2,$$

and as a by-product of the action of sulphur trioxide on carbon tetrachloride (see preparation of phosgene, $COCl_2$, p. 453) or on "sulphur monochloride," S_2Cl_2:

$$2SO_3 + CCl_4 = COCl_2 + S_2O_5Cl_2.$$
$$5SO_3 + S_2Cl_2 = 5SO_2 + S_2O_5Cl_2.$$

It is an oily liquid, which has a density of 1·87 at 0°, boils at 153°, and freezes at − 39°. It dissolves quietly in water, forming sulphuric and hydrochloric acids:

$$S_2O_5Cl_2 + 3H_2O = 2H_2SO_4 + 2HCl.$$

Sulphur Trioxide as an Oxidising Agent.

It has been shown above that sulphur dioxide is much more active as a reducing agent when water is present; conversely, sulphur trioxide is reduced to the dioxide most readily when dry or in concentrated solutions such as fuming or strong sulphuric acid. Whilst therefore dilute sulphuric acid behaves only as an acid and not as an oxidising agent, the concentrated acid, especially at high temperatures, begins to act as an oxidising agent, perhaps because it contains small quantities *of free sulphur trioxide.* Under these *conditions* sulphuric acid is reduced to sulphur dioxide by metals such as silver, mercury, and copper, by organic compounds such as olive oil and naphthalene,* by charcoal, by sulphuretted hydrogen, and finally by sulphur itself:

$$S + 2H_2SO_4 = 3SO_2 + 2H_2O.$$

* The oxidation of naphthalene (p. 446) by sulphuric acid was formerly the first stage in the preparation of artificial indigo; it was carried out in the presence of mercuric sulphate, which greatly facilitates the oxidation; the sulphur dioxide was recovered and used again.

Reduction of sulphuric acid also takes place when a bromide or iodide is acted upon by concentrated sulphuric acid:

$$2H_2SO_4 + 2KBr = SO_2 + Br_2 + K_2SO_4 + 2H_2O.$$
$$2H_2SO_4 + 2KI = SO_2 + I_2 + K_2SO_4 + 2H_2O.$$

Preparation of Sulphuric Acid by the Lead Chamber Process.

The LEAD CHAMBER PROCESS depends on passing a mixture of sulphur dioxide and air into large lead chambers into which steam and nitric acid vapour or oxides of nitrogen are also sent. The nitric acid or oxides of nitrogen are required only in small quantities and may be regarded as playing the part of a catalyst in the oxidation of sulphur dioxide and water to sulphuric acid. The presence of water is essential, and the product from the chambers is an aqueous acid containing about 68 per cent. of sulphuric acid, H_2SO_4.

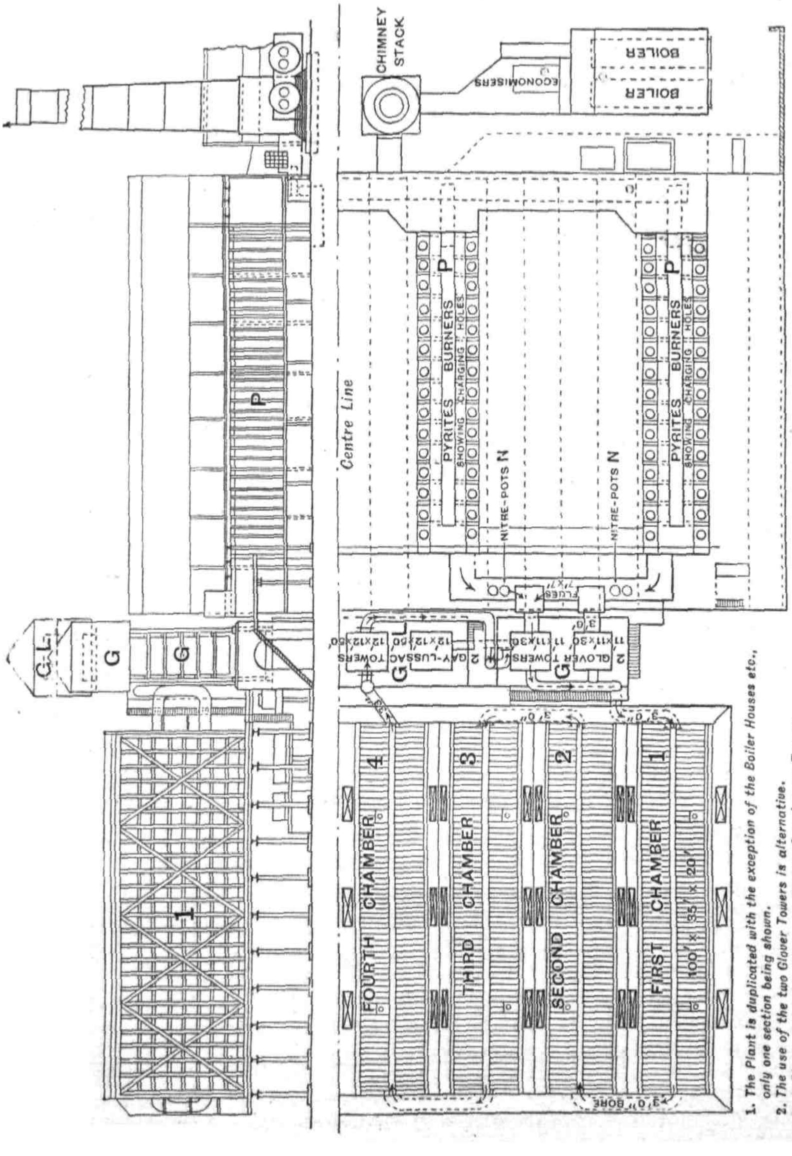
The sulphur dioxide used in the lead chamber process is usually prepared by burning iron pyrites,

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

The gas from the burners need not be purified and the action of the chambers is not impeded by the presence of arsenic. Lead chambers have therefore been erected in many cases to deal with noxious gases, produced by roasting sulphide ores of other metals, which were formerly allowed to escape into the air.

Nitric acid vapours, prepared by heating a mixture of nitre and concentrated sulphuric acid (or oxides of nitrogen prepared by oxidising a mixture of ammonia and air in contact with platinum gauze, p. 383), are introduced into the gases on their way to the chamber. The oxides of nitrogen in the spent gases from the lead chambers are absorbed by concentrated sulphuric acid in the GAY-LUSSAC TOWER, and are carried back into the chamber by hot gases from the burners meeting the "nitrous vitriol" in the GLOVER TOWER. Theoretically therefore the oxides of nitrogen are not used up in the process; but in practice they escape gradually from the lead chambers or are lost as gaseous nitrogen, N_2, or as nitrous oxide, N_2O, and must be renewed constantly.

A typical plant (Fig. 137) includes four wooden chambers, 1, 2, 3, and 4, of 70,000 cubic feet capacity each and lined with lead. Along the end of these are placed the burners (*P*) in which pyrites (50% S), "spent iron oxide" from the gas-works (40% S), or zinc blende (28% S) is roasted, fuel being required only in the last case. The hot gases from the burners pass first into a long flue, in which dust is deposited and into which nitric acid is distilled from nitre pots (*N*) standing in the flue. The gases are then led into the base of the Glover tower (*G*), a square shaft 11 feet × 11 feet × 30 feet high, packed with earthenware rings, over which trickles a mixture of chamber-acid with "nitrated" sulphuric acid from the Gay-Lussac tower described below. Dilution with weak chamber-acid liberates the oxides of nitrogen in the "nitrated" acid, and they are carried into the



1. *The Plant is duplicated with the exception of the Boiler Houses etc., only one section being shown.*
2. *The use of the two Glover Towers is alternative.*
3. *A Blower is provided between the two Gay-Lussac Towers.*

FIG. 137.—LEAD CHAMBER PLANT.

chamber by the hot gases, together with steam resulting from evaporation of the acid flowing down the tower. The gases pass by a flue into the first lead chamber and thence into the second, third, and fourth; in the first chamber, nitric oxide is present, but no higher oxides of nitrogen, since the gases are colourless; in the second chamber they are slightly red; and in the last, where the oxidation is complete, they are dark red. Steam from a boiler or a spray of finely divided water enters the chambers, and "chamber-acid" collects on the floors of the chambers.

The gases leaving the last chamber contain oxides of nitrogen together with much atmospheric nitrogen from the pyrites burners. They are sent up the Gay-Lussac tower (*G.L.*) and washed by means of concentrated acid (from the Glover tower) flowing down over layers of coke. The oxides of nitrogen are absorbed, probably in the form of nitrosulphonic acid, $NO_2{\cdot}SO_3H$, by the concentrated acid, and are recovered and returned to the chamber as described above, *i.e.*, by pumping the "nitrated acid" to the top of the Glover tower, diluting it with chamber-acid, and exposing the mixture to the hot gases from the burners. The function of the Gay-Lussac tower is therefore to prevent the loss of oxides of nitrogen, whilst the Glover tower serves (i) to return the oxides of nitrogen to the chamber, (ii) to cool the hot gases from the burners, (iii) to deprive the chamber-acid of water, and (iv) to remove from the chamber-acid any oxides of nitrogen which it may contain. The final product of the process is the partially concentrated acid collected at the base of the Glover tower.

Chemical Changes in the Lead Chamber.

Four principal theories have been advanced to account for the chemical changes which take place in the lead chamber, and in particular to explain the part played by the nitric acid or oxides of nitrogen in promoting the oxidation of sulphur dioxide.

(*a*) The simplest interpretation is that

(i) Nitric acid oxidises sulphur dioxide to sulphuric acid and is itself reduced to nitrogen peroxide, NO_2.

$$SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2 \quad \text{(i)}$$

(ii) The nitrogen peroxide oxidises a further quantity of sulphur dioxide to sulphuric acid, and is reduced to nitric oxide, NO.

$$SO_2 + NO_2 + H_2O = H_2SO_4 + NO \quad \text{(ii)}$$

(iii) Nitric oxide combines with atmospheric air and is reconverted to nitrogen peroxide, which acts again as in (ii).

$$2NO + O_2 = 2NO_2 \quad \text{(iii)}$$

The equations shown in (ii) and (iii) represent nitric oxide, NO, as taking oxygen from the air and passing it on to the sulphur dioxide; the nitric oxide is therefore alternately oxidised and reduced in the process, and is described as a CARRIER OF OXYGEN to the sulphur dioxide.

(*b*) A second theory suggests that **nitrosulphonic acid,** $HNSO_5$ or $NO_2{\cdot}SO_2{\cdot}OH$, is formed as an intermediate product. This compound is deposited on the walls of the chamber as white CHAMBER CRYSTALS when the supply of steam is not sufficient, but the crystals are decomposed at once on

admitting more steam. It is therefore suggested that the essential changes are :

$$HNO_2 + SO_2 = HNSO_5 \quad \ldots\ldots \quad (iv)$$
$$2HNSO_5 + H_2O = 2H_2SO_4 + NO_2 + NO \quad \ldots\ldots \quad (v)$$

the oxides of nitrogen are then reoxidised to nitric acid and interact with sulphur dioxide to give a further quantity of the nitrosulphonic acid :

$$NO_2 + NO + O_2 + H_2O + 2SO_2 = 2HNO_3 + 2SO_2 = 2HNSO_5 \quad (vi)$$

(*c*) Raschig has suggested that the intermediate product is not nitrosulphonic acid, $HNSO_5$ (which is not formed at the dilutions prevailing in the lead chamber), but a **nitrosisulphonic acid**, H_2NSO_5 (p. 387), containing one more atom of hydrogen, which breaks down into nitric oxide and sulphuric acid.

$$H_2O + NO_2 + SO_2 = H_2NSO_5 \quad \ldots\ldots \quad (vii)$$
$$H_2NSO_5 = H_2SO_4 + NO \quad \ldots\ldots \quad (viii)$$

(*d*) Divers suggests that the intermediate product is a **nitroxysulphuric acid**, $HO{\cdot}N\langle{}^{O}_{O}\rangle N{\cdot}SO_2{\cdot}OH$, or $H_2N_2SO_6$, containing an additional molecule of nitric oxide as compared with Raschig's compound. Its formation and decomposition are represented by the equation,

$$2HNO_2 + SO_2 = H_2N_2SO_6 = H_2SO_4 + 2NO \quad \ldots\ldots \quad (ix)$$

Concentration of Sulphuric Acid.

(*a*) Commercial oil of vitriol is concentrated by evaporation in lead pans until it contains 77 per cent. of H_2SO_4. Beyond this point lead dissolves rapidly in the hot acid, and further concentration is effected

(i) by distillation from platinum or glass retorts ;
(ii) by evaporation in CASCADES of basins of silica, or of acid-resisting cast iron, heated by a coke fire or by oil fuel (Fig. 138) ;
(iii) by passing hot gases over the surface of the dilute acid as in the KESSLER PLANT ;
(iv) by spraying it down a GAILLARD TOWER up which hot gases from the combustion of producer gas (p. 467) are passed.

In each case much acid is liable to be lost as " acid mist," but most of this can be condensed and recovered by coke-filters, and the residue by the COTTRELL PROCESS, in which the gas is exposed to an electrical potential of some 80,000 volts, arranged in a similar manner to a " brush-discharge," thus causing the fog to settle.

(*b*) Sulphuric acid is used on a very large scale for increasing the effective concentration of the nitric acid used in the " nitration " (p. 395) of cotton, glycerine, toluene, etc. These actions are accompanied by the liberation of water, which is absorbed by the sulphuric acid, *e.g.*,

$$\underset{\text{Glycerine}}{C_3H_8O_3} + 3HNO_3 = \underset{\text{Nitroglycerine}}{C_3H_5(NO_3)_3} + 3H_2O\,;$$

compare $$\underset{\text{Aluminium hydroxide}}{Al(OH)_3} + 3HNO_3 = \underset{\text{Aluminium nitrate}}{Al(NO_3)_3} + 3H_2O.$$

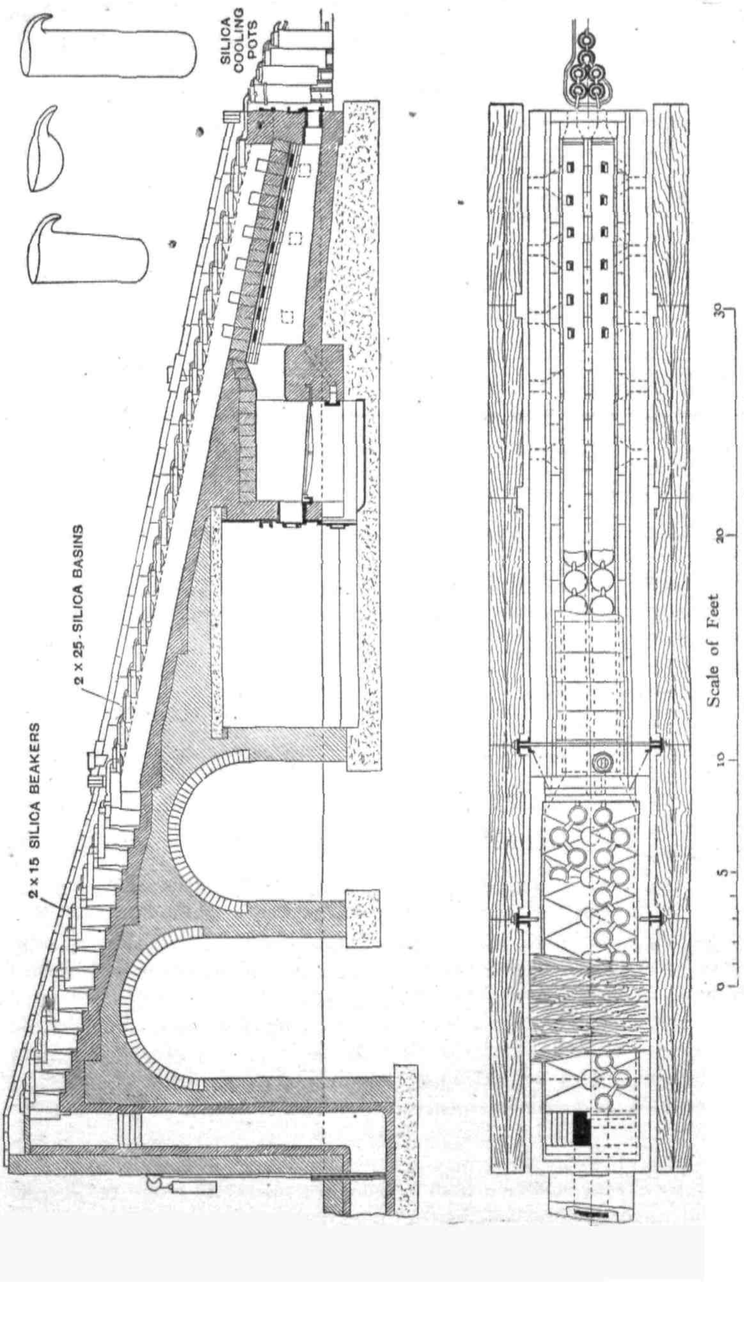


FIG. 138.—CASCADE FOR CONCENTRATION OF SULPHURIC ACID.

At the end of the process the "waste acids" are heated and diluted by superheated steam in order to release the oxides of nitrogen; the "denitrated acid" is then concentrated again in cascades or Gaillard towers and used for preparing a fresh quantity of "mixed acid" for nitration.

Commercial Purification of Sulphuric Acid.

Sulphuric acid prepared by the contact process is remarkably pure, but the acid prepared by the lead chamber process is liable to contain traces of lead sulphate, oxides of nitrogen, and arsenic. The first two impurities may be removed by distilling with a little ammonium sulphate, when the lead sulphate is left behind and the oxides of nitrogen are reduced to nitrogen gas:

$$(NH_4)_2SO_4 + N_2O_3 = 2N_2 + H_2SO_4 + 3H_2O.$$

The arsenic may be precipitated as sulphide by the action of sulphuretted hydrogen on the slightly diluted acid.

Properties of Sulphuric Acid.

As dilute sulphuric acid can be concentrated by evaporation or distillation only to 98·33 per cent. H_2SO_4 (b.-p. 330°), the commercial acid is usually of rather lower concentration, *e.g.*, 95 per cent. This acid takes up water greedily and can be used for drying all the common gases except ammonia, which is absorbed, and sulphuretted hydrogen, which is oxidised by the acid. The anhydrous acid of the composition H_2SO_4, known commercially as "monohydrate," was formerly prepared by freezing the strongest acid obtained by distillation, and draining the crystals on a centrifugal machine; at the present time such an acid would be prepared by mixing the commercial acid with fuming acid or "oleum" (p. 336), containing enough sulphuric anhydride to convert the water into sulphuric acid and so to produce an anhydrous sulphuric acid.

The anhydrous acid crystallises readily and melts at 10·4°. Its density is 1·848 at 15°, falling to 1·783 when the liquid is diluted to the composition represented by the formula H_2SO_4,H_2O. Very careful determinations have been made of the densities of solutions of known strength, prepared by mixing weighed quantities of crystalline sulphuric acid and of water, and these densities can be used to determine the strength of unknown acids, *e.g.*, a stock of acid can be tested in this way, and used very conveniently in the preparation of standard solutions of sulphuric acid by dilution with suitable quantities of water; a mixture prepared by diluting pure strong sulphuric acid with half its volume of water is generally used for the stock-acid, since the variations of concentration with density are relatively more rapid here than in a stronger or weaker acid. Pure sulphuric acid, as represented by the formula H_2SO_4, is a very poor electrical conductor, and would

perhaps be an insulator if no dissociation took place when the crystals are melted; an aqueous solution containing 30% H_2SO_4 is, however, one of the best electrolytic conductors, the specific resistance being only 1·4 ohms per centimetre cube (Fig. 136, p. 338).

Sulphuric acid is a strong acid with a powerful corrosive action, which depends largely on its power of dehydration, as when it converts sugar into charcoal,

$$C_{12}H_{22}O_{11} = 12C + 11H_2O;$$

in the case of the fuming acid, the oxidising properties of the sulphur trioxide increase still further the corrosive action of the acid.

Sulphuric acid is a "strong" acid, but in dilute aqueous solutions it is not so strong as hydrochloric acid. On account of its high boiling-point it will liberate hydrochloric acid from salt; but it is displaced in its turn when its salts are heated with silica, a compound which has only feeble acid properties but is very resistant to heat.

When heated strongly, sulphuric acid is decomposed as shown in the equation

$$2H_2SO_4 = 2H_2O + 2SO_2 + O_2.$$

Some of its salts break down in the same way when heated, *e.g.*,

$$2Al_2(SO_4)_3 = 2Al_2O_3 + 6SO_2 + 3O_2;$$

but some yield sulphur trioxide, as, for instance, ferrous sulphate, which was formerly heated in clay retorts to produce fuming or NORDHAUSEN OIL OF VITRIOL,

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3;$$

and some are strongly resistant to heat, as, for instance, Na_2SO_4, K_2SO_4, $MgSO_4$, and $CaSO_4$.

Disulphur Heptoxide or Persulphuric Anhydride, S_2O_7.

This compound was prepared by Berthelot, in 1877, in the form of long white needles, by passing electric sparks for ten hours through a dry mixture of sulphur dioxide and oxygen, or of sulphur trioxide and oxygen:

$$4SO_2 + 3O_2 = 2S_2O_7,$$
$$4SO_3 + O_2 = 2S_2O_7.$$

It sublimes readily at 10° and decomposes slowly into sulphur trioxide and oxygen. It was analysed by adding it to stannous chloride and estimating the amount of stannous chloride oxidised to stannic chloride and the quantity of sulphuric acid produced:

$$S_2O_7 + SnCl_2 + 2HCl + H_2O = SnCl_4 + 2H_2SO_4.$$

This oxide is the anhydride of per*di*sulphuric acid, $H_2S_2O_8$ (see below), which is formed when the oxide is dissolved in water; but the

solution decomposes rapidly with evolution of oxygen and formation of sulphuric acid.

$$S_2O_7 + H_2O = H_2S_2O_8; \quad 2H_2S_2O_8 + 2H_2O = 4H_2SO_4 + O_2.$$

The heptoxide oxidises sulphurous acid, potassium iodide, and ferrous sulphate in the cold, but has no action on oxalic acid, potassium permanganate, or ozone.

Persulphuric Acids.

Persulphuric acids are formed :—

(i) By dissolving disulphur heptoxide in sulphuric acid ;
(ii) By the electrolysis of sulphuric acid and of acid sulphates ;
(iii) By the action of hydrogen peroxide on sulphuric acid.

By these processes a series of persulphuric acids is produced, namely,

(*a*) Per*mono*sulphuric acid (Caro's acid), $H_2O_2,SO_3 = H_2SO_5$.
(*b*) Per*di*sulphuric acid (Marshall's acid), $H_2O_2,2SO_3 = H_2S_2O_8$.
(*c*) Per*tetra*sulphuric acid, $H_2O_2,4SO_3 = H_2S_4O_{14}$

Of these acids the best known is per*di*sulphuric acid, the salts of which are prepared and sold as commercial products (p. 581).

(*a*) **Permonosulphuric acid,** H_2SO_5, was isolated by d'Ans and Friederich in 1910, as a product of the action of chlorosulphonic acid (1 mol.) on hydrogen peroxide (1 mol.) :

$$H_2O_2 + ClSO_3H = H_2SO_5 + HCl.$$

The hydrogen chloride gas was pumped off and the per*mono*sulphuric acid was left as a crystalline residue melting at 45°. This acid was first discovered by Caro in specimens of potassium per*di*sulphate which had become acid by partial hydrolysis :

$$K_2S_2O_8 + H_2O = KHSO_5 + KHSO_4.$$

On neutralising with ammonium carbonate these acid samples of potassium persulphate (or artificial mixtures of potassium per*di*sulphate and sulphuric acid), the solutions were found by Caro to possess the unique property of oxidising aniline, $C_6H_5{\cdot}NH_2$, to nitrosobenzene, $C_6H_5{\cdot}NO$. They also possess the property of oxidising potassium iodide far more rapidly then the per*di*sulphates, and can even be estimated separately from the latter by rapid titration :

$$KHSO_5 + 2KI = K_2SO_4 + KOH + I_2.$$

This acid is monobasic, since when neutralised with chalk or an alkali and then decomposed by heat it liberates acid and oxygen in the proportions required by the equations

$$Ca(HSO_5)_2 = CaSO_4 + H_2SO_4 + O_2,$$
$$2NaHSO_5 = 2NaHSO_4 + O_2,$$

instead of remaining neutral as in the equations for salts of a dibasic acid :

$$2CaSO_5 = 2CaSO_4 + O_2,$$
$$2Na_2SO_5 = 2Na_2SO_4 + O_2.$$

(*b*) **Perdisulphuric acid,** $H_2S_2O_8$, like the *mono*-acid, was first isolated as a product of the action of chlorosulphonic acid (2 mols.) on anhydrous hydrogen peroxide (1 mol.) :

$$H_2O_2 + 2ClSO_3H = H_2S_2O_8 + 2HCl.$$

The hydrogen chloride was pumped off under reduced pressure and the acid obtained as a crystalline mass melting at 60°.

Salts of per*di*sulphuric acid can be prepared by electrolysing sodium hydrogen sulphate in contact with a small anode of platinum wire. The primary decomposition by the current is probably

$$NaHSO_4 = Na + \mathit{HSO_4}; \text{ compare } NaCl = Na + \mathit{Cl},$$

after which the HSO_4 groups liberated at the anode unite in pairs in exactly the same way as chlorine atoms :

$$2\mathit{HSO_4} = H_2S_2O_8; \text{ compare } 2\mathit{Cl} = Cl_2.$$

The perdisulphuric acid which results is a strong acid which can compete with sulphuric acid for the sodium present in the anode compartment and is probably present to a large extent in the form of sodium per*di*sulphate, $Na_2S_2O_8$. This salt is freely soluble in water, but the less soluble ammonium salt can be precipitated by adding ammonium sulphate to the solution, or the potassium salt can be prepared directly by electrolysing a solution of potassium hydrogen sulphate.

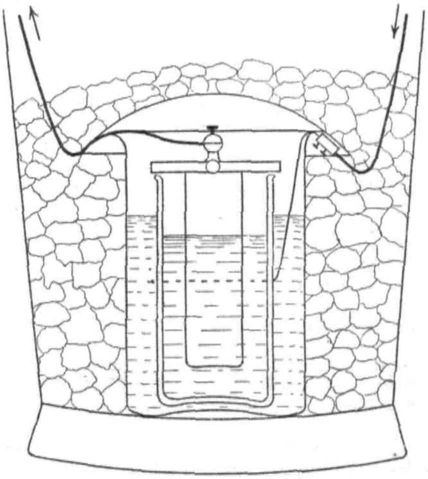


FIG. 139.—APPARATUS FOR THE PREPARATION OF PERSULPHURIC ACID.

Solutions containing perdisulphuric acid can be prepared by electrolysing 60 per cent. of sulphuric acid in contact with an anode composed of a single loop of platinum wire as in Fig. 139. The cathode consists of a sheet of platinum-foil enclosed in a porous pot, whilst the anode is a single turn of platinum wire wound round the porous pot. The whole apparatus is kept cold by placing it in a bucket filled with ice, the porcelain beaker containing the acid being covered with an inverted basin to keep out ice and ice-water.

The solutions prepared in this way are not stable and soon decompose with formation of per*mono*sulphuric acid, hydrogen peroxide, and finally gaseous oxygen :

$$H_2S_2O_8 + H_2O = H_2SO_4 + H_2SO_5.$$
$$H_2SO_5 + H_2O = H_2SO_4 + H_2O_2.$$
$$2H_2O_2 = 2H_2O + O_2.$$

Similar changes take place when the salts of per*di*sulphuric acid are acted on by sulphuric acid ; on dilution and neutralisation, the solutions are found to exhibit the oxidising properties of per*mono*sulphuric acid formed according to the equation

$$K_2S_2O_8 + H_2SO_4 + H_2O = H_2SO_5 + 2KHSO_4$$

(*c*) **Pertetrasulphuric acid,** $H_2S_4O_{14}$ or $(HS_2O_7)_2$, is related to pyrosulphuric acid, $H_2S_2O_7$, in the same way that per*di*sulphuric acid, $H_2S_2O_8$ or $(HSO_4)_2$, is related to sulphuric acid, H_2SO_4.

It has not been isolated, but when hydrogen peroxide is mixed with concentrated sulphuric acid the principal chemical change appears to be a balanced action in which the hydrogen peroxide interacts with four molecules of sulphuric acid as represented by the equation

$$H_2O_2 + 4H_2SO_4 \rightleftharpoons H_2S_4O_{14} + 4H_2O.$$

On dilution permonosulphuric acid is produced,

$$H_2S_4O_{14} + 3H_2O = H_2SO_5 + 3H_2SO_4.$$

It is probable that this acid is an intermediate product in the conversion of perdisulphuric acid into permonosulphuric acid by the successive action of sulphuric acid and water :

$$H_2S_2O_8 + 2H_2SO_4 = H_2S_4O_{14} + 2H_2O.$$
$$H_2S_4O_{14} + 3H_2O = H_2SO_5 + 3H_2SO_4.$$

Persulphuric Acids as Oxidising Agents.

The persulphuric acids are powerful oxidising agents, resembling hydrogen peroxide in many of their properties. Thus, they will all oxidise potassium iodide with liberation of iodine, *e.g.*,

$$H_2S_2O_8 + 2KI = 2KHSO_4 + I_2 \text{ (slow).}$$
$$H_2SO_5 + 2KI = K_2SO_4 + I_2 + H_2O \text{ (rapid).}$$
$$\text{compare } H_2O_2 + 2KI = 2KOH + I_2.$$

They will also convert ferrous sulphate into ferric sulphate :

$$2FeSO_4 + H_2S_2O_8 = Fe_2(SO_4)_3 + H_2SO_4,$$
$$2FeSO_4 + H_2SO_5 = Fe_2(SO_4)_3 + H_2O ;$$

but they differ from hydrogen peroxide in being without action on potassium permanganate. Some of these compounds are able also to dissolve metals and convert them directly into sulphates without liberation of hydrogen, *e.g.*,

$$Zn + H_2SO_5 = ZnSO_4 + H_2O.$$
$$Zn + Na_2S_2O_8 = ZnSO_4 + Na_2SO_4.$$

Other Oxy-acids of Sulphur.

Hyposulphurous acid, $H_2S_2O_3$, is formed in small quantities by direct combination of sulphurous acid and sulphur, but is very unstable, and when liberated from its salts decomposes as shown by the lower arrow in the equation

$$H_2O + SO_2 + S \rightleftharpoons H_2S_2O_3.$$

Hydrosulphurous acid, $H_2S_2O_4$, has been prepared in dilute solution by the action of oxalic acid on sodium hydrosulphite (p. 580), but decomposes rapidly, perhaps as shown in the equation

$$2H_2S_2O_4 + H_2O = H_2S_2O_3 + 2H_2SO_3 = 3H_2SO_3 + S.$$

Dithionic acid, $H_2S_2O_6$, is formed in small quantities when sulphurous acid is oxidised by potassium permanganate,

$$2H_2SO_3 + O = H_2O + H_2S_2O_6;$$

it can be separated from its barium salt by the action of dilute sulphuric acid and concentrated in a vacuum (compare $HClO_3$, p. 289), but it decomposes at higher concentrations as shown in the equation

$$H_2S_2O_6 = SO_2 + H_2SO_4.$$

Trithionic acid, $H_2S_3O_6$, **tetrathionic acid**, $H_2S_4O_6$, **pentathionic acid**, $H_2S_5O_6$, have also been prepared in solution; they are all unstable, breaking down readily into sulphurous and sulphuric acids and sulphur, but dilute solutions of the tetrathionic acid can be boiled without decomposition. A mixture of these acids was prepared in 1845 by passing hydrogen sulphide into sulphur dioxide and is known as WACKENRODER'S SOLUTION:

$$5H_2S + 5SO_2 = H_2S_5O_6 + 5S + 4H_2O.$$

SULPHUR AND THE HALOGENS.

Combination of Sulphur with the Halogens.

The affinity of sulphur for the halogens diminishes steadily in the series, fluorine, chlorine, bromine, iodine. With *fluorine* it forms a stable hexafluoride, SF_6. With *chlorine* it forms a tetrachloride, SCl_4, and a "monochloride," S_2Cl_2; a "dichloride" of the composition SCl_2 is a commercial product, but its chemical and physical properties indicate that it is perhaps a mixture of the two preceding compounds. With *bromine* sulphur forms a "monobromide," S_2Br_2, but it does not combine with *iodine*, the two elements separating completely on crystallisation when they have been melted together.

(*a*) **Sulphur hexafluoride**, SF_6, is formed by the direct combination of sulphur with fluorine. It is a colourless, odourless gas, which may be condensed to a colourless solid melting at $-55°$, and is a very stable compound.

(*b*) **Disulphur dichloride,** S_2Cl_2, *commonly known as* "*sulphur monochloride,*" is formed by passing chlorine over sulphur,

$$2S + Cl_2 = S_2Cl_2,$$

and is by far the most stable chloride of sulphur.

It is a yellow liquid of density 1·71 at 0°, boils at 138°, and freezes to a solid melting at − 76°. The molecular weight of this substance when dissolved in liquid chlorine corresponds with the formula assigned to it.

It readily dissolves sulphur, and the solution is used in the vulcanisation of rubber. Water decomposes it slowly, liberating sulphur,

$$2S_2Cl_2 + 3H_2O = 4HCl + H_2SO_3 + 3S.$$

It is used as a chlorinating agent in the preparation of carbon tetrachloride,

$$CS_2 + 2S_2Cl_2 = 3S_2 + CCl_4,$$

and by interaction with ethylene (p. 449) gives rise to "mustard gas" and sulphur,

$$S_2Cl_2 + 2C_2H_4 = S(C_2H_4Cl)_2 + S.$$

(*c*) **Sulphur tetrachloride,** SCl_4, is formed when chlorine is passed into disulphur dichloride at − 20° ; the yellow liquid which is first formed turns red, and becomes hot, when charcoal is added to promote the chlorination of the "monochloride." Sulphur tetrachloride is a brownish-red liquid which freezes to a yellowish-white solid melting at − 30°. It decomposes rapidly at atmospheric temperatures according to the equation

$$2SCl_4 = S_2Cl_2 + 3Cl_2.$$

Water decomposes it violently, forming sulphur dioxide and hydrochloric acid,

$$SCl_4 + 2H_2O = SO_2 + 4HCl.$$

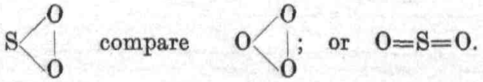
(*d*) **Disulphur dibromide,** S_2Br_2, is the only bromide of sulphur and is formed by the direct union of its elements. It is a red liquid which boils at 56° under 0·2 mm. pressure and with partial decomposition at 210° under atmospheric pressure. With water it gives sulphur dioxide, hydrobromic acid, and sulphur :

$$2S_2Br_2 + 2H_2O = SO_2 + 4HBr + 3S.$$

Valency of Sulphur and Constitution of Sulphur-compounds.

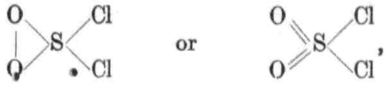
(*a*) *Compounds with Hydrogen and the Halogens.*—In hydrogen sulphide, SH_2, sulphur is clearly bivalent, but it is probably quadrivalent in the tetrachloride, SCl_4, and sexavalent in the hexafluoride, SF_6.

(*b*) *Sulphuryl Chloride and Sulphuric Acid.*—In sulphur dioxide, sulphur may be bivalent or quadrivalent, thus



Sulphur dioxide Ozone

Sulphuryl chloride, SO_2Cl_2, as an addition-compound of sulphur dioxide, may be written



making the sulphur either quadrivalent or sexavalent; the exact structure of the bivalent SULPHURYL RADICAL, SO_2, is not very important, and the compound is therefore often written as $SO_2{<}^{Cl}_{Cl}$. Sulphuric acid is produced by replacing chlorine in this compound by hydroxyl, —OH, and we may therefore write

$$SO_2{<}^{Cl}_{Cl} \qquad SO_2{<}^{Cl}_{OH} \qquad SO_2{<}^{OH}_{OH} \qquad SO_2{<}^{ONa}_{ONa}.$$

Sulphuryl chloride — Chlorosulphonic acid — Sulphuric acid — Sodium sulphate

The group $—SO_2·OH$, which is found in chlorosulphonic acid and in sulphuric acid, is called the SULPHONIC GROUP, and is present in many organic acids; *e.g.*, by acting on benzene, C_6H_6, with chlorosulphonic acid or with sulphuric acid we get **benzenesulphonic acid,** $C_6H_5·SO_2·OH$:

$$C_6H_6 + Cl·SO_2·OH \rightleftharpoons C_6H_5·SO_2·OH + HCl.$$
$$C_6H_6 + HO·SO_2·OH \rightleftharpoons C_6H_5·SO_2·OH + H_2O.$$

This group is assumed to be present, not only in chlorosulphonic acid and in sulphuric acid, but also in chamber crystals, or nitrosulphonic acid, $NO_2·SO_2·OH$, as well as in the very stable compound known as aminosulphonic acid, $NH_2·SO_2·OH$ (p. 389). Pyrosulphuric acid, $O{<}^{SO_2·OH}_{SO_2·OH}$, contains two sulphonic groups.

(*c*) *Sulphurous Acid and the Sulphites.*—Sulphurous acid may be written either as $H·SO_2·OH$ or as $O{=}S{<}^{OH}_{OH}$. The first formula shows a bivalent sulphuryl group, $—SO_2—$, united to hydrogen and to hydroxyl, and forming with the hydroxyl a true sulphonic acid; the second formula shows a SULPHOXIDE GROUP, —SO—, united to two hydroxyl radicals. Isomeric organic compounds derived from each of these formulæ are known, but it is not certain which type of formula should be assigned to sulphurous acid and the sulphites; it is even possible that the acid may have one formula and some of the salts another, *e.g.*,

$$O{=}S{<}^{OH}_{OH} \qquad SO_2{<}^{ONa}_{H} \qquad O{=}S{<}^{ONa}_{ONa}.$$

Sulphurous acid — Sodium hydrogen sulphite — Sodium sulphite

(*d*) *Thiosulphates.*—The sulphites unite readily with oxygen to form sulphates and with sulphur to form thiosulphates (p. 580). The latter are analogous to the sulphates, but contain —SNa in place of —ONa, thus:

$$SO_2{<}^{ONa}_{ONa} \qquad SO_2{<}^{SNa}_{ONa}.$$

Sodium sulphate — Sodium thiosulphate

This —SNa group is very active, and on removing the sodium in combination with iodine a tetrathionate is formed:

$$I_2 + 2NaS{\cdot}SO_2{\cdot}ONa = 2NaI + \begin{matrix} S{\cdot}SO_2{\cdot}ONa \\ | \\ S{\cdot}SO_2{\cdot}ONa. \end{matrix}$$

Sodium tetrathionate

(*e*) *Persulphuric Acids.*—The chemical properties of the persulphuric acids and their preparation from hydrogen peroxide can be explained at once by formulating them as mono- and di-sulphonic acids derived from hydrogen peroxide:

$$HO{\cdot}O{\cdot}SO_2{\cdot}OH \text{ and } HO{\cdot}SO_2{\cdot}O{\cdot}O{\cdot}SO_2{\cdot}OH.$$

Per*mono*sulphuric acid — Per*di*sulphuric acid

In these compounds the sulphonic groups alone possess acid properties, the —O·OH group of per*mono*sulphuric acid resembling hydrogen peroxide in being practically devoid of acid properties. The peroxide group —O·OH confers upon the mono-acid, however, a greater oxidising power than is possessed by the di-acid, in which the peroxide group —O·O— is locked away between two sulphonic groups. It will be noticed that sodium perdisulphate is analogous to sodium tetrathionate, but contains the PEROXIDE GROUP —O·O— in place of the DISULPHIDE GROUP —S·S—. The derivation of these salts from the sulphates and thiosulphates is also similar, as is shown in the equations

$$2NaO{\cdot}SO_2{\cdot}ONa = 2Na + (O{\cdot}SO_2{\cdot}ONa)_2,$$
$$I_2 + 2NaS{\cdot}SO_2{\cdot}ONa = 2NaI + (S{\cdot}SO_2{\cdot}ONa)_2,$$

the sodium being removed in the former case by electrolysis (usually of the acid sulphate) and in the latter case by the action of iodine.

Atomic Weight of Sulphur.

The atomic weight of sulphur is based upon Stas's determinations of the ratios

$$Ag_2SO_4 : 2Ag \text{ and } 2Ag : Ag_2S.$$

In more recent experiments the ratio

$$Ag_2SO_4 : 2AgCl$$

has been determined by passing hydrogen chloride over silver sulphate in a heated tube of silica-glass.

Detection and Estimation of Sulphur.

(*a*) Free sulphur may be detected by dissolving in caustic soda and testing the solution for sodium sulphide as follows :—

(i) A drop of the solution is placed on a silver coin ; sodium sulphide will produce a brown stain.
(ii) A solution of sodium nitroprusside, $Na_2Fe(CN)_5(NO)$, is added, which gives a purple colour with alkaline sulphides.
(iii) The solution is acidified with dilute sulphuric acid and added to a mixture of potassium thiocyanate, KCNS, and ammonium molybdate, $(NH_4)_2MoO_4$, dissolved in water ; sulphides give a violet or red colour, which is unaffected by ether.

(*b*) Substances containing sulphur may be heated to redness with an excess of metallic sodium in order to convert the sulphur into sulphide ; or the substance may be oxidised, *e.g.*, by bromine and fuming nitric acid, and the product tested for sulphuric acid.

(*c*) Sulphur is usually estimated by converting it to sulphuric acid and weighing as barium sulphate, $BaSO_4$, or as lead sulphate, $PbSO_4$.

34. Selenium, Se = 79·2
52. Tellurium, Te = 127·5.

Classification.

These two elements resemble sulphur in the same way that bromine and iodine resemble chlorine. They are therefore grouped with oxygen as members of an " oxygen family " of elements, corresponding with the four halogens as follows :—

8. Oxygen	=	16	9. Fluorine	=	19·0
16. Sulphur	=	32·06	17. Chlorine	=	35·46
34. Selenium	=	79·2	35. Bromine	=	79·92
52. Tellurium	=	127·5	53. Iodine	=	126·92

The halogens are all non-metals, but the elements of the oxygen family show an interesting gradation of properties, since whilst oxygen and sulphur are typical non-metals, tellurium has the appearance and characteristics of a metal resembling zinc; selenium, occupying an intermediate position between sulphur and tellurium, is known both in a metallic and in a non-metallic form.

Occurrence and Separation.

Selenium and tellurium are much less abundant than sulphur. They are found in small quantities in a free state and are distributed widely in combination with metals as selenides and tellurides corresponding with the metallic sulphides. These compounds are found occasionally as distinct minerals, *e.g.*, PbSe, Ag_2Se, Cu_2Se, $AuTe_2$, but occur much more frequently as isomorphous impurities in the corresponding sulphides, *e.g.*, copper pyrites, $CuFeS_2$, and iron pyrites, FeS_2.

Native tellurium had been known for a considerable time before Klaproth in 1798 confirmed the existence of the new element and named it tellurium (Latin, *tellus*, the earth). Selenium was discovered by Berzelius in 1817 as a red deposit in the flues and chambers of a sulphuric acid plant in which seleniferous pyrites was being used. On account of its analogy with tellurium he named it selenium (Greek, σελήνη, the moon).

(*a*) *Separation of Selenium.*—Selenium is separated from the red flue-dust described above by oxidising the element to selenic acid, H_2SeO_4, by means of nitric acid or potassium chlorate in presence of hot 50 per cent. sulphuric acid; the selenic acid is reduced to selenious acid, H_2SeO_3, by partial evaporation with hydrochloric acid of the filtered solution and separated from the residue of insoluble matter by decantation; the element is then precipitated from the cold clear solution by further reduction with sulphur dioxide. The crude product is freed from copper and lead by converting it into sodium selenate, Na_2SeO_4, by fusion with sodium carbonate and sodium nitrate and filtering off from the metallic impurities. Selenium can also be separated by extracting it from the crude material with potassium cyanide, probably as KCNSe (compare KCNS), and reprecipitating the element by the addition of hydrochloric acid.

(*b*) *Separation of Tellurium.*—Tellurium is separated from ores containing bismuth telluride, Bi_2Te_3, by heating with sodium carbonate and then extracting with water a mixture of sodium telluride, Na_2Te, with some sodium sulphide, Na_2S; from this solution tellurium separates as a grey powder on exposure to air. Tellurium can also be obtained as a by-product of the preparation of metallic bismuth and of the electrolytic refining of copper. The crude metal is purified by oxidation by aqua regia to tellurous acid, H_2TeO_3, filtered off from lead chloride, and reprecipitated by reduction with sulphur dioxide. It can also be purified by fusing the crude metal with potassium cyanide, extracting with water (perhaps as KCNTe, compare selenium) in the absence of air and reprecipitating by atmospheric oxidation. The metal can also be purified by distillation in a current of hydrogen.

Allotropy and Physical Properties.

(*a*) *Tellurium.*—METALLIC TELLURIUM is a brittle, silver-white metal closely resembling zinc both in its appearance and in its physical constants, *e.g.*:

	Density.	*Melting-point.*	*Boiling-point.*
Tellurium .	6·3	438°	red-heat
Zinc . .	7·1	419°	918°

It crystallises in the rhombohedral system, like arsenic, antimony, and bismuth, and is isomorphous with the metallic form of selenium. It can be precipitated from solution in an amorphous (or perhaps microcrystalline) form of slightly lower density (6·0); and from dilute solutions brown and blue colloidal solutions of the element have been obtained; but apart from this no other form of allotropy has been observed and no non-metallic form of the element is known.

(*b*) *Metallic Selenium.*—Selenium may resemble tellurium on the one hand or sulphur on the other, and therefore exhibits well-defined allotropy. The most stable form of the element is METALLIC SELENIUM, Se_{MET}, which is formed by heating any of the other forms at a temperature just below the melting-point. It melts at 217°, has a density of 4·8, and when sublimed in a sealed tube forms black rhombohedral crystals in which the right angles of the cube are distorted to about 87°, the corresponding angle for tellurium being 86° 47′. No corresponding form of sulphur is known. Metallic selenium conducts electricity: its electrical resistance is diminished by exposure to light, and this has been made use of in photometry and in schemes for the electrical transmission of pictures.

(*c*) *Non-metallic Selenium.*—(i) When precipitated selenium is allowed to stand in contact with carbon disulphide, alcohol, benzene, or chloroform, it is converted gradually into red monosymmetric crystals of NON-METALLIC OF SOLUBLE SELENIUM. These are probably isomorphous with S_{IV} or tabular sulphur, and may therefore be formulated as Se_{IV}. They melt at about 170° but readily change into the metallic form, melting at 217°. Their density, 4·47, is less than that of metallic selenium, and they appear to be less stable at all available temperatures, the transformation to metallic selenium being monotropic (p. 320) and not enantiotropic. In contact with selenium chloride or nitrogenous solvents, such as quinoline, C_9H_7N, and aniline, $C_6H_5{\cdot}NH_2$, amorphous selenium passes directly into the metallic form.

(ii) When selenium and sulphur are allowed to crystallise together, three series of solid solutions are formed. From 0 to 35 per cent. of selenium, these have the orthorhombic form of ordinary soluble sulphur, S_I; from 35 to 60 per cent. of selenium they have the monosymmetric form of nacreous sulphur, S_{III}; from 67 to 100 per cent. of selenium they have the monosymmetric form of tabular sulphur, S_{IV}, since this is the form of sulphur corresponding with non-metallic or soluble selenium.

(iii) Crystals of selenium corresponding with S_{II}, the common monosymmetric or prismatic form of sulphur, have not been prepared, either alone or as solid solutions, but crystals of a fourth monosymmetric type, which may be described as Se_V, have been prepared by crystallisation from carbon disulphide; these are dark red and semi-metallic in appearance and are perhaps intermediate between Se_{IV} and metallic selenium. In all, it appears that sulphur, selenium, and tellurium exhibit six crystalline types as follows:

S_I	(and isomorphous Se_I)	Orthorhombic
S_{II}		Monosymmetric
S_{III}	(and isomorphous Se_{III})	,,
S_{IV}	and Se_{IV}	,,
Se_V		,,
Se_{MET}	and Te_{MET}	Rhombohedral.

(*d*) *Amorphous and Colloidal Selenium.*—Like tellurium, selenium is usually precipitated in an amorphous (or perhaps microcrystalline) form, and dilute solutions may yield a colloidal solution of the metal on reduction. A *vitreous* form of the element is obtained as a brown glass of density 4·28 by rapid cooling of melted selenium.

(*e*) *Physical Properties and Vapour-density.*—Selenium boils at 690° and from 900° to 1800° has a vapour-density corresponding with the formula Se_2; from 900° down to the normal boiling-point, however, the vapour-density increases by about one-third. The molecular weight of selenium dissolved in white phosphorus corresponds with the formula Se_8. The vapour-density of tellurium from 1400° to 1800° corresponds with the formula Te_2.

Chemical Properties of Selenium.

Selenium has less affinity than sulphur both for hydrogen and for oxygen, the element being displaced by sulphur from its hydride as well as from its oxide; in this respect it resembles bromine, which has less affinity than chlorine both for hydrogen and for oxygen. The affinity of selenium for the halogens appears, however, to be greater than that of sulphur. The weak affinities of selenium bring it into line with the noble metals in some of its properties: thus in the electrolytic refining of copper (p. 830) both selenium and tellurium remain behind with silver and gold in the anode slime.

(*a*) *Selenium and Hydrogen.*—**Hydrogen selenide** or **seleniuretted hydrogen**, H_2Se, is a gas with an intolerable odour, which can be prepared (like hydrogen sulphide) by the action of hydrochloric acid on ferrous selenide, FeSe, or in a purer state by the action of water on aluminium selenide, Al_2Se_3. It is an endothermic compound,

$$H_2 + Se\ (cryst.) \rightleftarrows H_2Se\ (gas) - 25{,}000\ cal.,$$

and therefore tends to be formed in larger proportions as the temperature is raised. Below 300°, the action is slow and equilibrium is not readily attained, but at higher temperatures the proportion of H_2Se in the gas increases from 19 per cent. at 325° to 40 per cent. at 575°; it then appears to diminish again to about 35 per cent. at 750°.

Hydrogen selenide melts at −64° and boils at −42°. Its solutions redden litmus and precipitate the heavy metals in the form of SELENIDES (compare hydrogen sulphide).

(*b*) *Oxidation.*—Selenium burns in air with a blue flame and a characteristic odour of rotten horse-radish, giving **selenium dioxide**, SeO_2; this condenses in colourless needles and vaporises at about 300° without melting. The dioxide is decomposed by molten sulphur, liberating selenium, which is therefore usually carried forward as an element when seleniferous sulphur or pyrites is burnt. When dissolved in water, selenium dioxide gives **selenious acid**, H_2SeO_3, which crystallises out from solution in colourless prisms, but yields the dioxide and water when heated; it is a dibasic acid, yielding poisonous salts. The acid can be prepared by dissolving selenium in nitric acid, and is reduced again to selenium by sulphur dioxide, ferrous sulphate,

hydrogen iodide, hydrazine, hydroxylamine, and hypophosphorous acid (compare gold, p. 856). Potassium permanganate oxidises it quantitatively to **selenic acid,** H_2SeO_4, a dibasic acid analogous with sulphuric acid, which forms metallic SELENATES, which are analogous and isomorphous with the sulphates. Selenic acid was first prepared by oxidising selenium with chlorine-water,

$$Se + 3Cl_2 + 4H_2O = H_2SeO_4 + 6HCl.$$

Selenious acid can be oxidised in the same way, but this is a reversible action, since selenic acid is reduced to selenious acid by boiling with concentrated hydrochloric acid,

$$H_2SeO_3 + Cl_2 + H_2O \rightleftarrows H_2SeO_4 + 2HCl.$$

Barium selenate can also be distinguished from barium sulphate by its solubility in hydrochloric acid,

$$BaSeO_4 + 2HCl = BaSeO_3 + Cl_2 + H_2O.$$

The oxidising properties of the acid, which are shown by these actions to be comparable with or greater than those of chlorine, afford an explanation of the fact that selenic acid will dissolve gold as well as the baser metals.

(*c*) *Other Compounds.*—Selenium unites directly with the halogens to form

SeF_4	and SeF_6	compare *SF_6*
Se_2Cl_2	and $SeCl_4$	compare S_2Cl_2 and SCl_4
Se_2Br_2	and $SeBr_4$	compare S_2Br_2
Se_2I_2	and SeI_4	

The compounds shown in italics are gaseous.

Selenium tetrachloride interacts with the dioxide to form **selenyl chloride,** $SeOCl_2$,

$$SeCl_4 + SeO_2 = 2SeOCl_2;$$

this interacts with thionyl chloride, $SOCl_2$, its sulphur-analogue, to form selenium tetrachloride and sulphur dioxide,

$$SeOCl_2 + SOCl_2 = SeCl_4 + SO_2,$$

as might perhaps be expected in view of the fact that selenium has more affinity than sulphur for the halogens, but less for oxygen.

Selenium unites with sulphur trioxide to form **selenosulphur trioxide,** $SeSO_3$, which separates as a green solid (compare S_2O_3, which is blue); it also dissolves in neutral sulphites, *e.g.* K_2SO_3, to form SELENOSULPHATES such as **potassium selenosulphate,** K_2SeSO_3, which are isomorphous with the thiosulphates.

Chemical Properties of Tellurium.

Although the physical properties of tellurium are similar to those of zinc, its chemical properties are in general those of a non-metal, and show some resemblance to those of arsenic, another element which occupies an uncertain position in the classification of elements as metals and non-metals.

(*a*) *Tellurium and Hydrogen.*—**Tellurium hydride** or **telluretted hydrogen,** H_2Te, is formed along with hydrogen by the action of an acid on magnesium telluride,

$$MgTe + 2HCl = MgCl_2 + TeH_2,$$

or by electrolysing 50 per cent. sulphuric acid with a tellurium cathode. The liquid boils at 0° and freezes at −40°. The gas decomposes on exposure to light, and in contact with moist air, depositing metallic tellurium. Its preparation and properties show some analogy to those of arsine, AsH_3 (p. 702).

(*b*) *Oxidation.*—Tellurium burns in air to **tellurium dioxide,** TeO_2, which also separates in a crystalline form from solutions of tellurium in nitric acid. When distilled it solidifies to a colourless, crystalline mass. It is only slightly soluble in water and does not redden blue litmus. It yields acid-derivatives such as **tellurous acid,** H_2TeO_3 (precipitated by diluting a solution of tellurium in nitric acid), and the TELLURITES ; but it also forms a perchlorate, sulphate, and nitrate which are decomposed by water (compare the quadrivalent lead salts, p. 697) ; and it must therefore be classed as an amphoteric oxide (p. 529) having both acid and basic properties. Potassium permanganate oxidises the acid quantitatively to **telluric acid,** H_2TeO_4, a dibasic acid from which a series of TELLURATES is derived. **Potassium tellurate** can be prepared by fusing tellurium with potassium carbonate and nitrate or by oxidising potassium tellurite with chlorine water,

$$K_2TeO_3 + Cl_2 + H_2O = K_2TeO_4 + 2HCl.$$

The tellurium in this solution can be precipitated as **barium tellurate,** $BaTeO_4$, compare $BaSO_4$, and converted by the action of sulphuric acid into telluric acid. Ignition of telluric acid gives **tellurium trioxide,** TeO_3, which on stronger heating decomposes into the dioxide and oxgyen. **Tellurium monoxide,** TeO, is also known (see below).

(*c*) *Other Compounds.*—Tellurium forms the following halogen-compounds : TeF_4 and TeF_6, $TeCl_2$ and $TeCl_4$, $TeBr_2$ and $TeBr_4$, TeI_4. It unites with sulphur, instead of forming solid solutions, giving a **disulphide,** TeS_2, and a **trisulphide,** TeS_3. It also unites with sulphur trioxide to form **tellurium sulphoxide,** $TeSO_3$ (compare S_2O_3 and $SeSO_3$), a red solid which when heated loses sulphur dioxide and forms **tellurium monoxide,** TeO.

Atomic Weights.

The atomic weight of selenium was deduced from measurements of the ratios $Se : SeO_2 : Ag_2SeO_3$, $2Ag : Ag_2SeO_3$, $(NH_4)_2SeBr_6 : 6AgBr$, and from measurements of the density of H_2Se.

The atomic weight of tellurium is of special interest, since it was thought it should be less than that of iodine, whereas all measurements hitherto made show it to be greater. The ratios determined have been $K_2TeBr_6 : 6AgBr$, $TeBr_4 : 4AgBr$, $H_2TeO_4 : TeO_2 : Te$, and $Te(CH_3)_3Br : Ag$ or $Te(CH_3)_3I : Ag$.

CHAPTER XXVI

7. NITROGEN. N = 14·008

Occurrence of Nitrogen.

(*a*) *Atmospheric Nitrogen.*—Nitrogen is present in the free state in air, of which it forms 78 per cent. by volume or 75½ per cent. by weight. The residue left after removing the oxygen from air was described by Lavoisier as AZOTE (Greek, ἀ, not; ζωή, life), since it was not capable of supporting life; it is a mixture of nitrogen with 1/84 of its volume of argon and traces of other gases, and is now commonly described as ATMOSPHERIC NITROGEN.

(*b*) *Fixation of Nitrogen.*—Nitrogen is present only in very small proportions in the oceans and in the solid crust of the earth, but it is an essential constituent both of vegetable and of animal tissues. These are composed mainly of

(i) CARBOHYDRATES, such as cellulose and starch, $(C_6H_{10}O_5)_n$, which have the empirical composition of compounds of carbon and water and contain no nitrogen;

(ii) PROTEINS, which are complex compounds built up from AMINO-ACIDS containing nitrogen linked with hydrogen, in much the same way as in ammonia.

The carbohydrates are derived from the carbon dioxide of the air with the help of sunlight, and serve as foodstuffs for animals, which are unable to effect this reduction. Even plants, however, are not as a rule able to build up their nitrogenous constituents directly from atmospheric nitrogen, and must be provided with this element in the form of combined or FIXED NITROGEN, *e.g.*, nitrogen which has been brought into solution in the water of the soil in the form of ammonium salts or of nitrates; the fixed nitrogen may also be provided as complex organic compounds in decaying vegetable or animal matter, from which nitrogen is released, mainly in the form of ammonia, for further use by plants. In view of the essential character of nitrogen as a constituent both of plants and of animals, and of the constant wastage of fixed nitrogen by reversion to nitrogen gas, the problem of the artificial FIXATION OF NITROGEN is of great importance for the maintenance of food supplies; special interest attaches therefore to the modern methods of fixing atmospheric nitrogen by combination either with hydrogen (p. 378) or with oxygen (p. 404), in addition to the cognate problem of

making the best use of the nitrogen already fixed in the soil, in peat and in coal. This nitrogen was probably "fixed" in the first instance by electrical discharges in the air; but certain bacteria growing on the roots of clover and of some related plants are able also to absorb and use atmospheric nitrogen and so to increase directly the stock of fixed nitrogen in the soil.

Preparation of Nitrogen.

(*a*) *From Air.*—Crude nitrogen can be separated from air by any process which serves to remove from it the oxygen which it contains. Thus, air may be passed over copper, which is oxidised thereby but can be reduced again to the metallic state by some cheap gaseous fuel such as producer gas (p. 467). Producer gas itself may be used to give a mixture of nitrogen and hydrogen by removing the oxides of carbon which it contains. The main source of nitrogen is, however, the distillation of liquid air (p. 373), which may be carried out in such a way as to give pure nitrogen and impure oxygen or pure oxygen and impure nitrogen. The process can also be carried out in such a way as to recover and make use of the argon and other inactive constituents of the air.

(*b*) *From Compounds of Nitrogen.*—Nitrogen can be prepared by the oxidation of ammonium salts (pp. 382 and 600), *e.g.*, by heating a mixture of ammonium sulphate and potassium nitrite, when ammonium nitrite is formed, but breaks down into nitrogen and water:

$$(NH_4)_2SO_4 + 2KNO_2 = K_2SO_4 + 2NH_4NO_2$$
$$NH_4NO_2 = N_2 + 2H_2O.$$

It was Lord Rayleigh's discovery that nitrogen prepared by chemical methods was less dense than atmospheric nitrogen that led to the discovery of argon and the other inert gases of the atmosphere.

Physical Properties of Nitrogen.

Nitrogen is a colourless, odourless gas, which condenses to a liquid that boils at $-196°$, and freezes to a colourless solid melting at $-210{\cdot}5°$. The boiling-point is below, and the freezing-point above, that of oxygen: there is therefore no difficulty in freezing the liquid by evaporation under reduced pressure.

The gas is sparingly soluble in water, which dissolves 2 per cent. of its volume of the gas at 8°, as compared with 4 per cent. of oxygen.

Chemical Properties of Nitrogen.

(*a*) *Gaseous Nitrogen as a Stable Compound.*—Gaseous nitrogen is a very inactive substance, which does not interact with any of the ordinary chemical agents at atmospheric temperatures, although it has been stated that traces of ammonium nitrite are produced by direct combination of nitrogen with water in sunlight,

$$N_2 + 2H_2O = (NH_4)NO_2.$$

This inactivity must be attributed to the great stability with which the two atoms of nitrogen are combined together in the molecule, and disappears when the molecule is broken down. Thus, when a high-tension arc is passed through air an unstable modification of nitrogen is produced, which can be oxidised to nitrogen peroxide by the action of ozone, but soon reverts to the ordinary inactive form of the element. The ACTIVE NITROGEN prepared by Strutt by the action of a high-tension discharge on nitrogen under reduced pressure is even less inert. The product converts sodium and mercury into nitrides, the mercury nitride being explosive; during this action line-spectra of the metals are developed. The active gas converts acetylene and chloroform into cyanogen, perhaps according to the equations

$$C_2H_2 + 2N = C_2N_2 + H_2$$
$$2CHCl_3 + 2N = C_2N_2 + 2HCl + 2Cl_2.$$

It has no action on hydrogen, and is rendered inactive by oxygen without being oxidised. With nitric oxide it forms nitrogen trioxide, which can be condensed as a blue solid by liquid air; this apparent oxidation of nitric oxide by nitrogen may be attributed to the formation of diatomic nitrogen thus,

$$2NO + N = N_2 + NO_2 \text{ and } NO + NO_2 = N_2O_3,$$

compare the action of fluorine on nitric oxide (p. 407),

$$4NO + F_2 = N_2 + 2NO_2F.$$

The reversion of active nitrogen to the ordinary form is accompanied by a glow which can be checked by heating the gas, but reappears as it cools.

(*b*) *Combination with Nitrogen.*—At higher temperatures nitrogen will interact with several elements and compounds, *e.g.*,

(i) *Hydrogen* will unite with nitrogen when sparked in presence of sulphuric acid, or when the compressed mixture is passed over heated iron at 500°.

(ii) *Oxygen* unites with nitrogen, under the influence of the electric discharge, forming nitric oxide; but the compounds with *halogens* can only be prepared by indirect methods and are explosive.

(iii) *The metals* magnesium, calcium, and lithium combine directly with nitrogen to form **magnesium nitride**, Mg_3N_2, **calcium nitride**, Ca_3N_2, and **lithium nitride**, Li_3N. Cerium and uranium burn with brilliant incandescence when ignited in nitrogen.

(iv) *Calcium carbide* absorbs nitrogen, forming calcium cyanamide (pp. 477 and 626) and carbon:

$$\underset{\text{Calcium carbide}}{CaC_2} + N_2 = \underset{\text{Calcium cyanamide}}{CaCN_2} + C.$$

Barium carbide, on the other hand, forms barium cyanide:

$$\underset{\text{Barium carbide}}{BaC_2} + N_2 = \underset{\text{Barium cyanide}}{BaC_2N_2}.$$

The compounds of nitrogen with hydrogen and with oxygen are described in two following sections. The compounds with halogens are described, as substitution-derivatives, under ammonia. The compounds with halogens and oxygen are described under nitric and nitrous acids, from which they are derived by replacement of hydroxyl by halogens.

THE ATMOSPHERE.

Constituents of Air.

From very early times air was regarded as an element. The presence of **water vapour** was recognised at an early date, but this was not regarded as an essential part of the air.

The first evidence that air was really complex was therefore found in the fact that its volume was diminished by mice breathing and by substances burning in air over water (Mayow, 1674), and that the residue was unfit for further combustion or for respiration. The presence in air of the principal product of combustion or respiration, namely **carbon dioxide,** was recognised in 1755 by Black, who gave to this gas the name of "fixed air."

Priestley (1772), Scheele (1774), and Lavoisier (1774) showed that diminution of volume to the extent of one-fifth could be brought about by a large number of different agents, *e.g.*,

(i) By burning metals such as tin, lead, and mercury, or non-metals such as charcoal, sulphur, and phosphorus, in air.

(ii) By the action at atmospheric temperatures of rusting iron, of ferrous salts (especially when converted into ferrous hydroxide, $Fe(OH)_2$, by the addition of alkali), of iron filings and sulphur, or of iron pyrites weathering to green vitriol; or

(iii) By the action of alkaline sulphides such as the liver of sulphur prepared by dissolving sulphur in potash or in lime, and of sulphites formed by dissolving in an alkali the fumes of burning sulphur.

The active part of the air which was removed by these agents was recovered by Priestley in 1774 from the red calx formed by heating mercury gently in air and was described by Lavoisier as **oxygen.**

Priestley found that a larger diminution could be produced by sparking air, and Cavendish (1784) showed that, when mixed with an excess of oxygen and sparked over potash, the whole of the air could be converted into saltpetre with the exception of a small quantity not exceeding 1/120 of the whole. The constituent of air which was thus converted into nitre by combination of oxygen and potash was described by Chaptal in 1792 as **nitrogen** (Greek, *νίτρον*, saltpetre or nitre; *γεννάω*, I become).

The small bubble of gas which was not absorbed in Cavendish's experiment was regarded for more than a century as nitrogen which had remained unabsorbed on account of its extreme dilution with oxygen. About 1890, Lord Rayleigh, who was engaged in an accurate

redetermination of the density of the commoner gases, found that "atmospheric nitrogen" was denser than nitrogen prepared by chemical methods from nitric oxide, nitrous oxide, ammonium nitrite, or urea. The density of "atmospheric nitrogen" was increased by allowing some of it to escape by diffusion, but chemical methods were used by Rayleigh and Ramsay in order to separate the denser constituents in a pure state. This was done (i) by repeating Cavendish's experiment on a larger scale, and (ii) by absorbing by means of heated magnesium the nitrogen from 160 litres of atmospheric nitrogen. The density of the gas relatively to hydrogen was thus increased from 14 to 19·78, and the new gas, on account of its extreme inertness, was described as **argon** (Greek, ἀ, not; ἔργον, work).

Subsequent investigations showed that this residue also was a mixture of 5 inert gases, namely, **helium, neon, argon, krypton,** and **xenon.**

The Inert Gases of the Atmosphere.

The residue of air left after absorbing the water-vapour, carbon dioxide, oxygen, and nitrogen, consists principally of argon; but when air is liquefied in large quantities it is possible by fractional distillation to separate from it two gases, *helium* and *neon*, which boil at lower temperatures than nitrogen and oxygen, and two other gases, *krypton* and *xenon*, which boil at higher temperatures. *Argon*, boiling at a temperature between the boiling-points of oxygen and nitrogen and only 3° below the boiling-point of oxygen, is associated mainly with this gas.

These five gases are characterised by their complete inertness; they give rise to no chemical compounds, and their valency is therefore taken as zero. Measurements of the ratio of the specific heats in argon and helium have shown that the molecules of these gases are monatomic, as in the case of mercury-vapour. The atomic weights and the physical properties of the elements are shown in the following table:

TABLE 42.—PHYSICAL PROPERTIES OF THE HELIUM GROUP OF ELEMENTS.

	Atomic weight.	*Melting-point.*	*Boiling-point.*
Helium . . .	4·00	—	− 269°
Neon . . .	20·2	− 253° (?)	− 239°
Argon . . .	39·88	− 188°	− 186°
Krypton . . .	82·92	− 169°	− 152°
Xenon . . .	130·2	− 140°	− 109°

(*a*) *Helium*.—The existence in the sun of a new element, for which the name helium (Greek ἥλιος, the sun) was proposed, was suggested by Lockyer and by Janssen in 1868 in order to account for a line in the solar spectrum which could not be attributed to any terrestrial element. The gas was first isolated by Ramsay in 1895 from the mineral CLEVEITE, which had been thought previously to liberate nitrogen when heated

or when dissolved in sulphuric acid. It has since been obtained as a product of the disintegration of radium salts, and is present in nearly all radioactive minerals, as well as in the gases which escape from radioactive water, *e.g.*, in the mineral springs of Bath. Helium is present in the air to the extent of about 5 parts per million and remains behind when all other constituents are condensed by charcoal cooled with liquid hydrogen ; it has recently been separated in large quantities in America from natural gas with a view to fill airships, since, although its density is twice as great and its lifting power only 92 per cent. of that of hydrogen, it has the advantage of not being inflammable. The gas was liquefied by Onnes in 1908 and has been used extensively in his laboratory at Leiden as a cooling agent in experiments at very low temperatures. The liquid boils at 4·5° absolute, and does not crystallise even when cooled to 3° absolute by evaporation under reduced pressure ; it is the only element which has not yet been obtained in the solid state.

(*b*) *Neon* (Greek νέος, new) is present in the air to the extent of about 15 parts per million, but its spectrum is so brilliant that it can be detected in the gas remaining from 1/100 c.c. of air when the other constituents (with the exception of helium) have been condensed by charcoal cooled in liquid air.

(*c*) *Argon*, which is present to the extent of 0·933 per cent. in air or 1·18 per cent. in atmospheric nitrogen, can be separated from liquid air as a commercial product, and has found an important use as a filling for " half-watt " lamps. In these lamps the tungsten filament, instead of being in a vacuum, is enclosed in an atmosphere of an inert gas ; the temperature of the hot filament can then be increased by about 500° without " blackening " the glass bulb. The dissociation of a diatomic gas at the temperature of the filament gives rise to excessive cooling, and in order to secure the highest efficiency a monatomic gas must be used, and argon has been found to be the most suitable gas for this purpose.

(*d*) *Krypton* (Greek, κρύπτω, I hide) and (*e*) *Xenon* (Greek, ξένος, a guest or stranger), which are present only in minute traces in air, are of interest mainly as additional members of this remarkable family of inert elements.

Composition of Air.

In addition to variable quantities of water-vapour and of carbon dioxide, air contains the following constituents :

TABLE 43.—COMPOSITION OF AIR.

Per cent. by volume after drying.

Nitrogen	=	78·111	Helium	=	0·0005
Oxygen	=	20·955	Hydrogen	=	0·0001
Argon	=	0·933	Krypton	=	0·000005
Neon	=	0·0015	Xenon	=	0·0000006

(*a*) *Water*.—The proportion of water in the atmosphere varies greatly from time to time. The maximum amount depends on the temperature; thus at 30° water-vapour may contribute 32 mm. to the total pressure, at 15° the maximum vapour pressure is 12·79 mm., and at 0° it is 4·58 mm. Below the freezing-point the amount of moisture in the air depends on the sublimation-pressure of ice (p. 8) and soon becomes extremely small. It is for this reason that, in cold climates, fires are specially dangerous in winter, when everything becomes extremely dry through the almost perfect condensation of moisture; in a Canadian winter even calcium chloride ceases to be deliquescent, and becomes efflorescent instead. Again, one of the easiest and most effective ways of drying air is by cooling it.

The proportion of moisture in the air can be determined accurately by passing a known volume of air through a series of weighed tubes containing sulphuric acid or phosphoric oxide to absorb the moisture, and measuring the increase in weight which is thus produced. It can be estimated rapidly by determining the DEW-POINT, that is, the temperature at which liquid water begins to condense on a bright surface. Thus, air which deposits dew at 8° contains water-vapour at a pressure of 8·046 mm., and would be 8·046/12·790 = 63 per cent. saturated at 15°, when the maximum vapour pressure of water is 12·790 mm. The dryness of the air may also be determined roughly with the help of a pair of "wet and dry bulb" thermometers, arranged so that the temperature of one bulb is lowered by the evaporation of water, whilst the other records the prevailing temperature of the air; thus, in the case just described of air with a dew-point of 8°, if the reading of the dry bulb were 15°, the wet bulb would be cooled by evaporation to about 11°; tables have been compiled whereby the proportion of moisture in the air can be deduced from these two readings.

(*b*) *Carbon Dioxide*, CO_2.—The proportion of carbon dioxide in air may be determined (i) gravimetrically, by absorption in potash from a very large volume of air, say 40 litres (compare the gravimetric estimation of moisture), or (ii) volumetrically by PETTENKOFER'S METHOD, in which a known volume of air (say 10 litres) is shaken with a standard solution of baryta to absorb the carbon dioxide, and the excess of baryta is estimated by titrating it against a standard solution of oxalic acid, using phenolphthalein as indicator.

The proportion of carbon dioxide in normal air is about 3 parts in 10,000 by volume; in large towns the proportion sometimes rises to 6 parts in 10,000, and in crowded rooms 30 parts in 10,000 may be found. The proportion of carbon dioxide in air is often used as a measure of its purity, but it must not be supposed that carbon dioxide is itself harmful, in view of the high proportion which is always present in the lungs. Even 3 or 4 per cent. of carbon dioxide in air does not interfere with respiration to any great extent, and the oppressiveness of the air

of a crowded room is due mainly to its saturation with moisture and to the absence of draughts, producing a dull, monotonous atmosphere in which the refreshing stimulus to the skin by cooling and evaporation is entirely eliminated.

(*c*) *Oxygen.*—The proportion of oxygen in air was first estimated by Priestley by mixing equal volumes of nitric oxide and air over water in a graduated tube, which he called a EUDIOMETER (Greek εὐδία, fair weather, εὔδιος, fair or clear; μέτρον, a measure), and measuring the contraction which took place. Much more accurate results were obtained by exploding a mixture of hydrogen and air over mercury in a VOLTA'S EUDIOMETER (compare Fig. 114, p. 253), provided with two metallic points for use in producing a spark in the gas; as 2 volumes of hydrogen combine with 1 volume of oxygen to form liquid water, one-third of the contraction after the explosion is due to oxygen. Still more exact measurements were made by Dumas in 1841 by a gravimetric

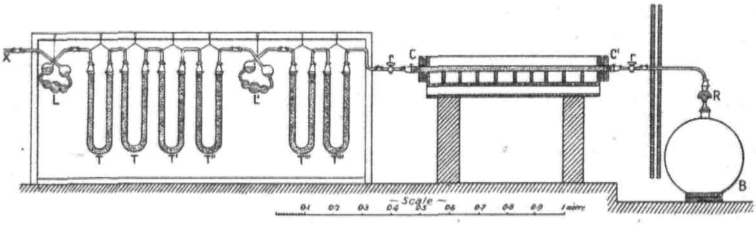


FIG. 140.—APPARATUS FOR DETERMINING THE GRAVIMETRIC COMPOSITION OF AIR. (Dumas and Boussingault.)

X = tube for admission of air. *L* = Liebig potash-bulbs. *TT* = pumice moistened with potash. *T'* = potash in fragments. *T''* = ignited potash in fragments. *L'* = sulphuric acid in Liebig bulbs. *T'''* *T''''* = pumice moistened with strong sulphuric acid. *CC'* = hard glass tube filled with copper reduced from oxide. *rr* = taps for use in evacuating tube. *B* = large globe into which nitrogen flows on opening the tap *R*.

method in which air freed from moisture and carbon dioxide was admitted into a vacuous tube filled with red-hot copper in order to remove the oxygen, whilst the nitrogen passed forward into an empty globe and was weighed directly (Fig. 140). In one experiment 3·680 grams of oxygen were absorbed by the copper, leaving a residue of 12·304 grams of nitrogen in the globe and 0·069 gram of nitrogen in the copper oxide tube. The ratio of oxygen to nitrogen was therefore 3·680 : 12·373 or oxygen : nitrogen = 22·92 : 77·08 per cent.

As an average of many experiments the proportion of oxygen by volume is found to be almost exactly 21 per cent., but varies slightly in different localities. Allowing for the presence of 0·933 per cent. by volume of argon, the composition of the air, after removing water-vapour and carbon dioxide, is:

	By volume.	By weight.
Oxygen	20·96	23·2
Nitrogen	78·11	75·5
Argon	0·93	1·3
	100·00	100·0

(*d*) *Other Constituents.*—The proportion of argon in air was determined by measuring the total residue of inert gases and deducting the proportions found by other methods for helium, neon, krypton, and xenon. The proportion of helium was determined by condensing out all the other constituents in charcoal cooled by liquid hydrogen. The proportions of neon and hydrogen were determined in a similar manner by condensing the less volatile constituents of air in charcoal cooled by liquid air and separating the hydrogen from the neon by chemical methods. The proportions of helium and neon found in this way agree fairly closely with those which can be recovered when air is fractionally distilled on a large scale, namely 15 and 5 parts per million. The proportions of krypton and xenon are those found in the last residues left by the evaporation of liquid air.

Air a Mixture.

That air is a mixture and not a compound is proved

(i) By the fact that its composition does not correspond with any definite chemical formula, even when the minor constituents are regarded as impurities.

(ii) By the small variations in the proportions of nitrogen and oxygen which are found in different localities and at different times.

(iii) By the fact that the composition of air can be altered and its constituents separated mechanically by diffusion through a porous membrane.

(iv) By the change of composition which occurs when air is dissolved in water and separated again by boiling.

(v) By the fractional distillation of liquid air, which gives no evidence of the presence of chemical compounds.

(vi) By the absence of any marked change of volume, or liberation or absorption of heat, when the constituents are mixed to give a product having just the same properties as natural air.

Liquefaction of Air.

Compressed air is liquefied by making use of the cooling effect produced either

(i) By expansion against the internal attraction of the molecules, as in the Hampson and Linde processes, or

(ii) By expansion in an engine doing work, as in the Claude process.

In each case the liquefaction depends on a system of REGENERATIVE COOLING whereby the compressed air entering the plant is cooled by the expanded air coming from the plant, so that the cooling effects are accumulated in the gas.

(*a*) In the HAMPSON PROCESS, as shown diagrammatically in Fig. 141, air freed from carbon dioxide by the action of lime in a " low-pressure purifier " is compressed to about 200 atmospheres, separated from condensed water, freed from the last trace of carbon dioxide by passing over potash in a " high-pressure purifier," and cooled regeneratively by the escaping gases, which freeze out all the moisture in the compressed air and reduce its temperature considerably. The air is then expanded

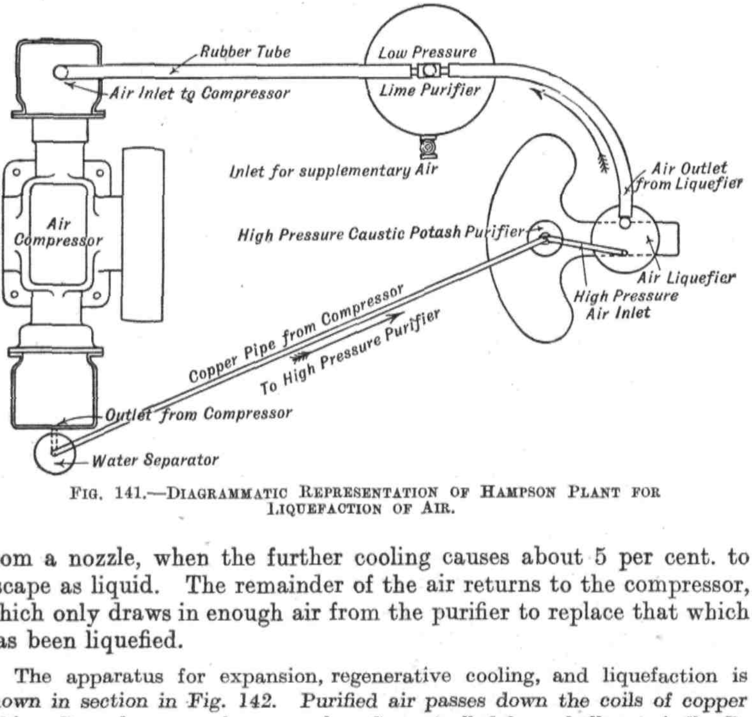


FIG. 141.—DIAGRAMMATIC REPRESENTATION OF HAMPSON PLANT FOR LIQUEFACTION OF AIR.

from a nozzle, when the further cooling causes about 5 per cent. to escape as liquid. The remainder of the air returns to the compressor, which only draws in enough air from the purifier to replace that which has been liquefied.

The apparatus for expansion, regenerative cooling, and liquefaction is shown in section in Fig. 142. Purified air passes down the coils of copper tubing *B*, and escapes from a valve *C*, controlled by a hollow spindle *D*, which can be turned by means of a milled head at *E*. The expanded gas from the valve *C* passes over the coils *B* and escapes at *F*, at the point where air is drawn in to the compressor. Liquid air collects in the receiver *G* and can be drawn off through the tube *R* by turning the handle *T* and thus opening the valve *P*. The liquid air is received and stored in vacuum-jacketed Dewar vessels (Fig. 143), in which conduction of heat is minimised by mounting the tube or flask inside an outer jacket; convection is prevented by removing the air from the space between the two walls, and radiation is reduced by silvering

the walls enclosing the vacuous space. In vessels of this type the liquid gas can be stored for hours or even days with only a slow loss by evaporation.

(*b*) In the LINDE PROCESS;

(i) The purified air is cooled to $-35°$ at a comparatively small cost by the evaporation of liquid ammonia (as in an ordinary

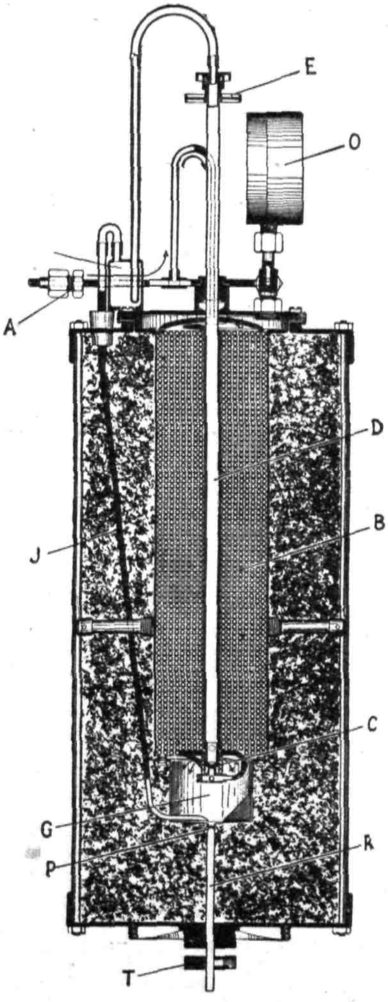
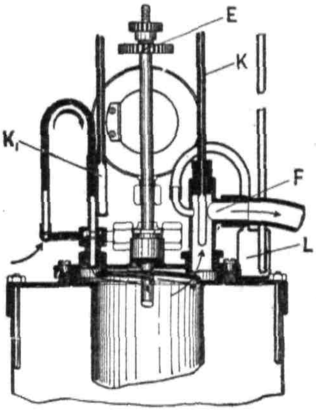


FIG. 142.—HAMPSON APPARATUS FOR LIQUEFACTION OF AIR.



ice-producing plant) before making use of the main cooling effect of the expanded gases.

(ii) Air is liquefied much more economically by expansion in a closed circuit from 200 to 50 atmospheres only; the liquid air produced in this way is passed through a valve into a vessel under atmospheric pressure, where it evaporates until it has cooled to the normal boiling-point: some liquid air is lost in this process, but the cold gases are made use of to cool the main supply of air and so are not entirely wasted.

As a result of these improvements, the yield of liquid air is multiplied by 3 and amounts to about 0·65 litre per kilowatt-hour.

(c) In the CLAUDE PROCESS, for which a still higher efficiency is claimed, purified air at 40 atmospheres pressure is cooled to − 140° by expanding to a pressure of about 4 atmospheres in an engine which is coupled up to assist in driving the compressor. The cold gases escaping from the engine are used to liquefy some of the compressed air, the boiling-point of which under 40 atmospheres pressure is about −140°. The liquid air is released from 40 atmospheres to atmospheric pressure, but the cold gases which then escape are also used to cool the compressed air.

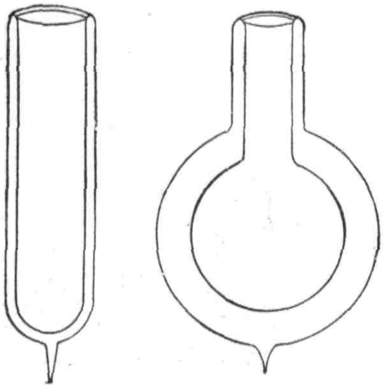


FIG. 143.—VACUUM-JACKETED DEWAR VESSELS, FOR COLLECTING AND STORING LIQUEFIED GASES.

Properties of Liquid Air.

Liquid air is a *pale blue*, mobile liquid, of density 1·0 approximately. It boils between − 183° and − 196°, according to its composition. Its latent heat of evaporation is only about 50 calories per gram, as compared with 536 calories for water.

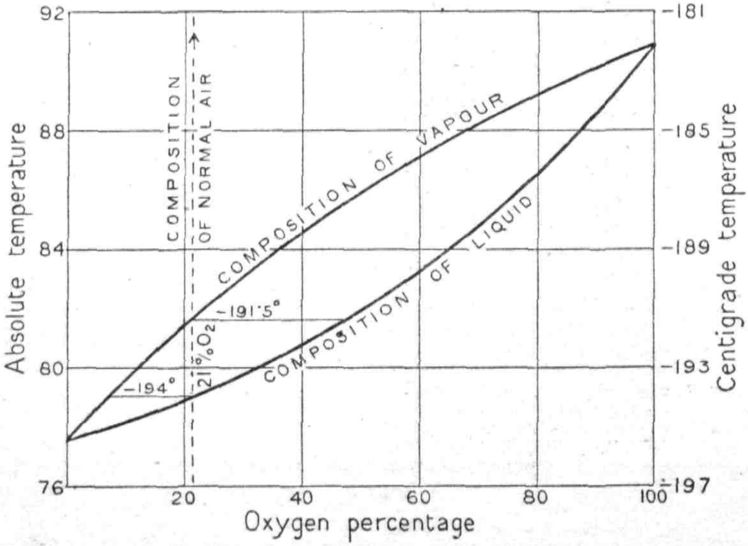


FIG. 144.—BOILING-POINTS OF LIQUID AIR.

The composition of liquid air boiling at different temperatures is shown by the lower curve in Fig. 144, whilst the composition of the vapour which

escapes from it is found by drawing a horizontal line across to the upper curve in this figure. This diagram may also be used to determine the temperature at which a liquid of given composition boils or a gas of given composition begins to condense. Thus, it will be seen that a liquid containing 21 per cent. of oxygen begins to boil at − 194° and gives off a gas containing only 7 per cent. of oxygen, whilst a gas containing 21 per cent. of oxygen begins to condense at − 191·5° and deposits a liquid containing about 48 per cent. of oxygen.

Liquid air is of great value as a cooling agent. It usually contains about 50 per cent. of oxygen, and this proportion increases on storage as the nitrogen is more volatile ; it can therefore be vaporised and used as an enriched air for respiration. When mixed with charcoal it forms a blasting explosive which has been used extensively and has certain marked advantages. The principal use, however, is in the commercial preparation of nitrogen, oxygen, and argon, as described in the following paragraph.

Fractional Distillation of Liquid Air.

(*a*) *Separation of Oxygen.*—In order to separate oxygen and nitrogen from liquid air, the liquid air plant is modified so that the compressed air is cooled, not only by the escaping gases, but also *by passing through coils immersed in the reservoir of liquid air* (Fig. 145) ; whilst, therefore, a pressure of 135 atmospheres is required to start up the plant, liquefaction soon takes place under a pressure of 50 to 60 atmospheres only. The liquid air in the reservoir *B* is evaporated by the coils of compressed air d_1, but does not boil as a uniform mixture, since nitrogen tends to boil off first and oxygen to accumulate in the reservoir. The fresh liquid formed from the compressed air is not delivered directly into the reservoir, but is sprayed into the top of a column or separator, *A*, serving as a " still-head," down which it flows by a zigzag path to the reservoir. During its passage down the column, the liquid meets the gases which have boiled off from the reservoir, and an interchange of constituents takes place, whereby almost the whole of the nitrogen is boiled off from the liquid before it reaches the reservoir, which therefore accumulates almost pure oxygen. A gas containing more than 99 per cent. of oxygen can in fact be drawn off from the bottom of the column. The oxygen drawn off at e_1, and the nitrogen drawn off at *F*, are finally removed at *E* and *C* after passing through the coils in counter-current to the compressed air which enters at *D*.

(*b*) *Separation of Nitrogen.*—The gas escaping at the top of the column in Fig. 145 is in equilibrium with liquefied air of normal composition containing 21 per cent. of oxygen, and therefore contains 7 per cent. of oxygen (Fig. 144). In order to prepare pure nitrogen, the process is modified, as in Fig. 146, so as to secure a further fractionation of this crude nitrogen. For this purpose the initial supply of air

(cooled by direct refrigeration and by the escaping gases) is passed under low pressure through a series of large coils, d_1, in the reservoir of liquid air, liquefied, and delivered halfway up the fractionating column at *A*, so that the zone in which the liquid contains 21 per cent. and the gas 7 per cent. of oxygen is brought down from the top of the column to this point. The high-pressure circuit f, f_1, f_2 is fed with crude nitrogen withdrawn from the top of the column through the coiled pipes, *CC*. A cumulative rectification then takes place, the liquid delivered at the

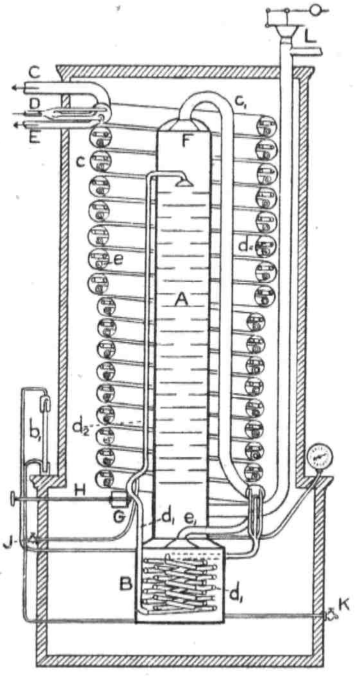


FIG. 145.—APPARATUS FOR SEPARATION OF OXYGEN FROM AIR. (After Greenwood.)

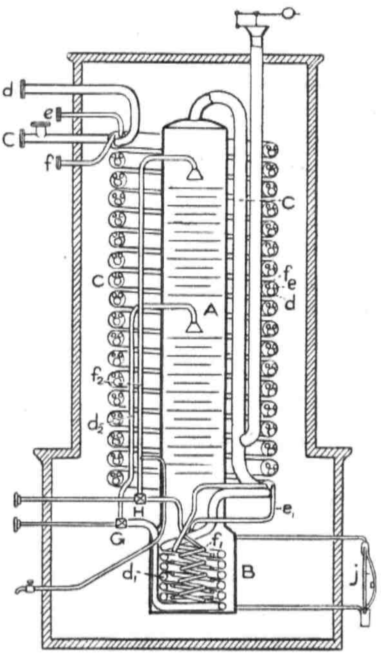


FIG. 146.—APPARATUS FOR SEPARATION OF NITROGEN FROM AIR. (After Greenwood.)

top of the column from the high-pressure coils becoming progressively richer in nitrogen until in steady working a gas containing about 99·5 per cent. of nitrogen can be drawn off.

(*c*) *Separation of Inert Gases.*—The less volatile gases, helium and neon, which are not liquefied in the high-pressure coils, can be concentrated up to 50 per cent. by cooling in the coldest part of the column whilst still under a pressure of 4 atmospheres, when most of the nitrogen is condensed. The nitrogen and other less volatile gases can be removed by absorption in charcoal at − 100°, when a mixture of

3 volumes of neon and 1 volume of helium is obtained; this can be separated by condensing the neon in charcoal at − 180°. Krypton and xenon tend to accumulate in the reservoir or to boil off with the oxygen. Argon, boiling only 3° below oxygen, tends to pass off mainly with the oxygen but partly with the nitrogen. By working under slightly different conditions, at a rather lower temperature, it can be condensed with the oxygen and separated from it by further fractionation.

(*d*) *Cost of Working.*—The process of fractionating liquid air may be regarded as one in which atmospheric air is fed into a machine and then withdrawn in the form of its constituent gases, *e.g.*, in Fig. 145, air is fed in at *D*, and emerges as nitrogen and oxygen at *C* and *E*. By the system of heat-interchange, the gases which escape are but little colder than the air which enters. The cost of working depends mainly (i) on the difference of temperature between these gases, (ii) on the leakage of heat into the apparatus. These represent a steady consumption of liquid air, in addition to the stock required to run the process. In practice, 1 litre of liquid air is lost in this way in the fractionation of about 30 litres.

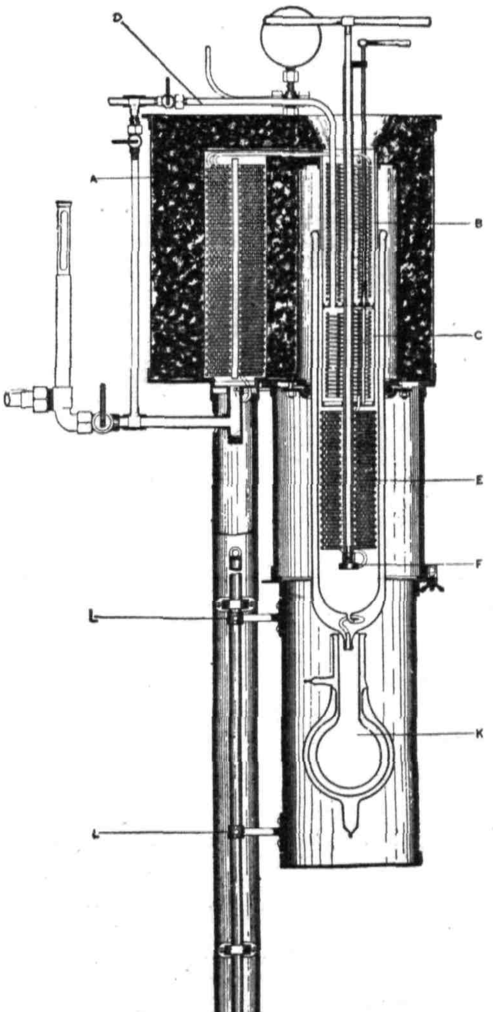


FIG. 147.—APPARATUS FOR LIQUEFACTION OF HYDROGEN.

Liquefaction of Hydrogen.

When hydrogen is expanded at atmospheric temperatures it becomes hotter instead of cooler (p. 130), but this behaviour is reversed at low temperatures. Hydrogen can therefore be liquefied by the cooling effect produced by its own expansion, if the compressed gas is first cooled by means of liquid air. The apparatus used for this purpose is shown in Fig. 147.

Hydrogen compressed, after purification, to 200 atmospheres passes successively through copper coils at *A*, *B*, *C*, and *E*. At *A* it is cooled by cold uncondensed hydrogen returning to the gas-holder. At *B* it is cooled by air boiling under atmospheric pressure at $-190°$. At *C*, liquid air from *B* is allowed to drip into a vacuous space, where it boils under reduced pressure at $-200°$, the evaporated air being drawn off through the tube *D*. At *E* the compressed hydrogen is cooled regeneratively by the expanded hydrogen escaping from the valve *F*, which soon begins to deliver liquid.

The whole of the expansion-system is enclosed in a large cylindrical Dewar vessel, and the Dewar flask *K* in which the hydrogen is collected is provided with two independent vacuum-jackets. The apparatus shown in Fig. 147 produces liquid at the rate of about 2 litres per hour.

Helium, boiling at $-269°$, has been liquefied in a similar manner, by its own expansion after preliminary cooling with liquid hydrogen.

NITROGEN AND HYDROGEN.

Hydrides of Nitrogen.

Nitrogen forms the following series of hydrides :—

Ammonia, NH_3.
Hydrazine, N_2H_4.
Azoimide or hydrazoic acid, N_3H.
Ammonium azide, $NH_3 + N_3H = N_4H_4$.
Hydrazine azide, $N_2H_4 + N_3H = N_5H_5$.

The two compounds richest in hydrogen, namely, **ammonia**, NH_3, and **hydrazine**, N_2H_4, are basic substances which dissolve in water to form alkaline solutions, and unite with acids to form salts ; this property of forming salts by direct combination with acids is shared also by **hydroxylamine**, NH_3O, an oxidised hydride which resembles ammonia in many of its properties, thus :

$$\underset{\text{Ammonia}}{NH_3} + HCl = \underset{\text{Ammonium chloride}}{NH_3,HCl \text{ or } NH_4Cl}.$$

$$\underset{\text{Hydrazine}}{N_2H_4} + 2HCl = \underset{\text{Hydrazine hydrochloride}}{N_2H_4,2HCl \text{ or } N_2H_6Cl_2}.$$

$$\underset{\text{Hydroxylamine}}{NH_3O} + HCl = \underset{\text{Hydroxylamine hydrochloride}}{NH_3O,HCl \text{ or } NH_4OCl}.$$

The salts derived in this way by direct combination of ammonia with acids are described as AMMONIUM SALTS, the COMPOUND-RADICAL or

group of atoms, NH_4 (which occupies the place of the SIMPLE RADICAL or metallic atom in salts such as sodium chloride, NaCl, compare p. 190), being known as AMMONIUM (p. 381).

The third hydride, **azoimide** or **hydrazoic acid**, N_3H, possesses strong acid properties, and unites with bases to form salts which are known as AZIDES; two of these, formed by combination with ammonia and with hydrazine, have the formulæ N_4H_4 and N_5H_5 and are therefore entitled to rank as hydrides of nitrogen.

Preparation of Ammonia.

(*a*) *From Sal-ammoniac.*—Ammonia has long been known in the form of its hydrochloride, **ammonium chloride** or SAL-AMMONIAC, NH_4Cl, a salt-like substance, first obtained by the distillation of camels' dung, which differs from ordinary salts in that it can be vaporised very readily. When distilled with an alkaline carbonate, it yields the volatile solid alkali, SAL VOLATILE, but when distilled with lime (Fig. 148), or with a caustic instead of a mild alkali, it gives a pungent gas which dissolves in water to form a strongly alkaline liquid. This liquid was first prepared by distilling horn in a retort and is still known as SPIRIT OF HARTSHORN; the gas was collected in a free state by Priestley in 1777 and was described by Bergman in 1782 as **ammonia**.

(*b*) *From Gas Liquor.*—When organic materials, such as peat, wood, or coal, are distilled, a considerable amount of the nitrogen escapes in the form of ammonia. Many tons are thus obtained from the aqueous GAS-LIQUOR produced by the distillation of coal (p. 465). The ammonia is distilled out, after adding a little lime to the solution to decompose any ammonium salts that may be present, and is then combined with sulphuric acid and put on the market, mainly for use as a fertiliser, in the form of **ammonium sulphate**,

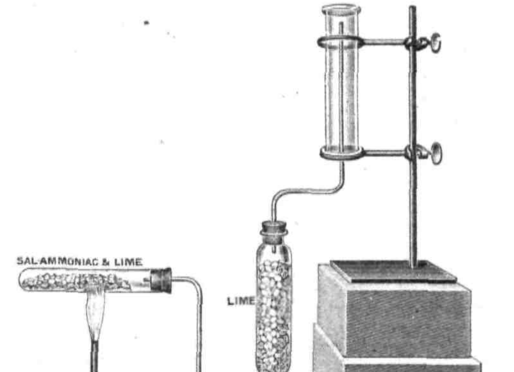


FIG. 148.—PREPARATION OF AMMONIA FROM SAL-AMMONIAC. The gas is dried with quicklime and collected in an inverted gas-jar.

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

Pure ammonia can be recovered from this ammonium sulphate by heating it with quicklime,

$$(NH_4)_2SO_4 + CaO = CaSO_4 + 2NH_3 + H_2O;$$

compare the earlier method of preparation by the action of lime on sal-ammoniac,

$$2NH_4Cl + CaO = CaCl_2 + 2NH_3 + H_2O.$$

The gas can be collected over mercury or by displacement of air, or may be condensed and stored as a liquid.

(c) *From Nitrogen and Hydrogen.*—The decomposition of ammonia into its elements by sparking was discovered by Priestley and used by Berthollet in 1785 to establish the volumetric composition of the gas (p. 135). St. Clair Deville, in 1865, showed that the decomposition is not complete, as Berthollet had supposed, since a cloud of sal-ammoniac was always produced when hydrogen chloride was added, even after long sparking. By sparking in presence of hydrogen chloride he was able to reconvert the mixture of nitrogen and hydrogen completely into sal-ammoniac; this recombination may also be demonstrated very conveniently by sparking a mixture of the two gases over concentrated sulphuric acid.

The combination of nitrogen and hydrogen is an exothermic process:

$$N_2 + 3H_2 = 2NH_3 + 2 \times 12{,}000 \text{ calories};$$

the decomposition of ammonia therefore becomes more complete when the temperature is raised. Thus, whilst the proportion of ammonia in equilibrium with its elements at atmospheric pressure is about $\frac{1}{4}$ per cent. at 450°, it diminishes to 1/20 per cent. at 600°. The combination is therefore far more difficult to effect than that of sulphur dioxide and oxygen (p. 334), which gives about 66 per cent. of sulphur trioxide even at 600°, but it is assisted greatly by working under pressure, as is shown in the following table:

TABLE 44.—COMBINATION OF NITROGEN AND HYDROGEN.

	Equilibrium-percentage of Ammonia at			
Temperature.	1 atm.	50 atm.	100 atm.	200 atm.
450°	0·24	9·5	16·2	25·3
500	0·13	5·7	10·4	17·6
550	0·08	3·7	6·9	12·0
600	0·05	2·3	4·5	8·2

Although a higher proportion of ammonia is obtained at 450°, the action is so slow that the working temperature has been fixed at 550°, as this gives a maximum output of ammonia from a given weight of catalyst. At this temperature only 0·08 per cent. of ammonia would be formed at atmospheric pressure, but in the HABER PROCESS (Fig. 149)

this proportion is increased to 12 per cent. by working under a pressure of 200 atmospheres, whilst Claude by raising the pressure to 1000 atmospheres secured a yield of 40 per cent. of ammonia by passing the gas once over the catalyst. The ammonia is condensed as a liquid by refrigeration, or in the Claude process by merely cooling with cold water, or is absorbed under pressure by water, or by anhydrous cobalt chloride. The residual gases are made to circulate constantly over the catalyst, the material removed in the form of ammonia being replaced by nitrogen derived from liquid air (p. 373) and hydrogen derived from water-gas (p. 468).

The best catalyst appears to be metallic iron, but this must be specially prepared and purified to free it from traces of sulphur. This is effected by melting the catalyst in an oxy-hydrogen flame, using alternatively an oxidising and a reducing atmosphere. The product is

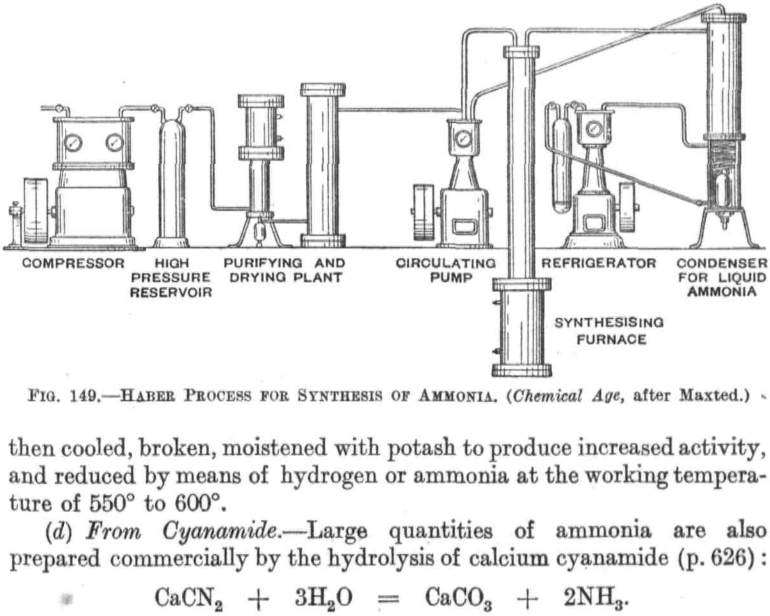


FIG. 149.—HABER PROCESS FOR SYNTHESIS OF AMMONIA. (*Chemical Age*, after Maxted.)

then cooled, broken, moistened with potash to produce increased activity, and reduced by means of hydrogen or ammonia at the working temperature of 550° to 600°.

(*d*) *From Cyanamide.*—Large quantities of ammonia are also prepared commercially by the hydrolysis of calcium cyanamide (p. 626):

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3.$$

The black powder is wetted to decompose any unchanged calcium carbide, and is hydrolysed in autoclaves holding 6 tons of water and 3 tons of cyanamide. Steam is passed in under a pressure of 3 atmospheres, and any acetylene set free at this stage is allowed to escape; the ammonia is then driven out by increasing the pressure of steam gradually to 11 atmospheres and the temperature to 180°.

(*e*) *By the Reduction of Nitric Acid.*—Ammonia can be produced on a small scale by the reduction of oxides of nitrogen. Thus, when a

nitrate is heated with zinc dust and caustic soda, or with aluminium and caustic soda, it is reduced to ammonia,

$$NaNO_3 + 4Zn + 7NaOH = \underset{\text{Sodium zincate}}{4Na_2ZnO_2} + NH_3 + 2H_2O.$$

This reduction is used as a qualitative test for nitric acid, but is not commercially practicable, as the products are of less value than the raw materials.

Physical Properties of Ammonia.

(*a*) *Gas.*—Ammonia is a light, pungent gas, its density being little more than half that of air. The rapid diffusion of the gas, consequent upon its low density, has been used to prove the presence of free ammonia in the vapour of sal-ammoniac (p. 600).

(*b*) *Liquid.*—Ammonia condenses readily to a liquid boiling at — 33° under atmospheric pressure; its vapour pressure at 10° is 6 atmospheres. The liquid is used on a large scale in refrigerating plants; the gas is liquefied by pressure, the temperature being kept down by jacketing the compressors with cold water; the liquid is then allowed to vaporise under the low pressure caused by the suction of the compressors, and the cooling produced by the vaporisation is used for the preparation of ice or for similar purposes.

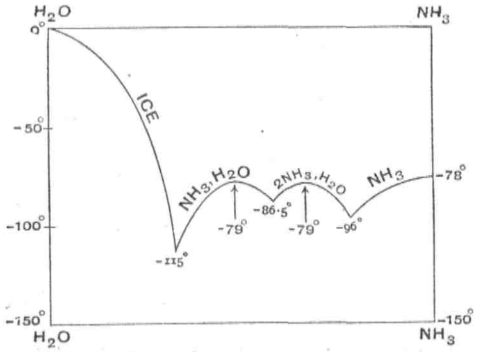


FIG. 150.—EQUILIBRIUM-DIAGRAM FOR AMMONIA AND WATER.

(*c*) *Solid.*—Ammonia freezes to a solid melting at —78°. It is remarkable that this freezing-point is within 1° of those of the two hydrates of ammonia shown in Fig. 150.

(*d*) *Ammonia and Water.*—Ammonia dissolves readily in water, which at 0° absorbs 1300 volumes of the gas, giving a solution containing nearly 50 per cent. of ammonia. The saturated solution contains 40 per cent. of ammonia at 11° and 33⅓ per cent. of ammonia at 22°. From solutions which are too concentrated to be preserved under normal conditions of temperature and pressure two hydrates can be crystallised out (Fig. 150), namely,

Ammonium hydroxide, NH_3,H_2O or $(NH_4)OH$, melting at — 79°.
Ammonium oxide, $2NH_3,H_2O$ or $(NH_4)_2O$, also melting at — 79°.

Chemical Properties of Ammonia.

The chemical properties of ammonia include :—

(i) *Addition, e.g.,* $NH_3 + HCl = NH_4Cl.$

(ii) *Substitution, e.g.,* $NH_3 + 3Cl_2 = NCl_3 + 3HCl.$

$2NH_3 + 2Na = 2NH_2Na + H_2.$

(iii) *Decomposition* with separation of nitrogen.

(*a*) *Ammonium Salts.*—The most important property of ammonia is the power which it possesses of uniting with acids to form AMMONIUM SALTS in which the AMMONIUM RADICAL, NH_4, plays the part of a univalent metal. It should be noticed that ammonia will combine directly with an *acid hydride,* just as a basic oxide will combine with an acid oxide, to form a ternary salt containing three elements, *e.g.*, ammonium chloride, NH_4Cl, or magnesium sulphate, $MgSO_4$; but it will only form a salt with an *acid oxide* when water is present to convert the ammonia into ammonium hydroxide or the oxide into a hydrogen acid, the product being a quaternary salt containing four elements, *e.g.*, ammonium sulphate, $N_2H_8SO_4$.

Two hydrides, $NH_3 + HCl = NH_4Cl.$

Two oxides, $MgO + SO_3 = MgSO_4.$

Hydride and oxide,

$$2NH_3 + H_2O + SO_3 \begin{cases} \nearrow (NH_4)_2O + SO_3 \searrow \\ \searrow 2NH_3 + H_2SO_4 \nearrow \end{cases} (NH_4)_2SO_4.$$

In the case of carbon dioxide, however, a salt, known as **ammonium carbamate,** $(NH_3)_2CO_2$, or $NH_2{\cdot}CO{\cdot}O{\cdot}NH_4$ (p. 604), is formed by direct combination with ammonia, whilst combination with ammonia in presence of water gives **ammonium carbonate,** $(NH_4)_2CO_3$. Again, whilst ammonia and sulphur trioxide unite in presence of water to form **ammonium sulphate,** $(NH_4)_2SO_4$, as set out above, in the absence of water they form two complex salts, $(NH_3)_3(SO_3)_2$ or $NH(SO_3NH_4)_2$ and $(NH_3)_4(SO_3)_2$ or $NH_4{\cdot}N(SO_3NH_4)_2$, which are described below (p. 389).

(*b*) *Action of Sodium and Potassium.*—Liquid ammonia dissolves metallic sodium and potassium, probably forming loose *addition*-compounds such as NH_3Na and NH_3K. When, however, ammonia gas is passed over heated sodium or potassium, *substitution* takes place, hydrogen is liberated, and the ammonia becomes fixed in the form of **sodamide,** $NaNH_2$, or **potassamide,** KNH_2. It should be noted that in this action hydrogen is displaced by a metal, and that ammonia gas, unlike ammonium hydroxide, here displays acid rather than basic properties.

Sodamide, $NaNH_2$, is a white substance which melts at 155° and sublimes at 400° with slight decomposition. It is hydrolysed by water, forming ammonia and caustic soda,

$$NaNH_2 + H_2O = NaOH + NH_3.$$

Sodamide is used as a reagent in the laboratory and in manufacturing operations, often as a substitute for metallic sodium.

(*c*) *Action of Chlorine.*—By the action of an excess of chlorine, ammonia is converted (by substitution of chlorine for hydrogen) into **nitrogen trichloride**, NCl_3:

$$NH_3 + 3Cl_2 = NCl_3 + 3HCl.$$

This is an oily liquid which detonates violently on the slightest provocation. The violent explosion of this compound must be attributed to the affinity of chlorine atoms for chlorine atoms and of nitrogen atoms for nitrogen atoms, since the only products formed are the molecules of these elements,

$$2NCl_3 = N_2 + 3Cl_2.$$

When ammonia is in excess, chlorine merely removes the hydrogen and liberates one-third of its volume of nitrogen,

$$8NH_3 + \underset{3\ vols.}{3Cl_2} = \underset{1\ vol.}{N_2} + 6NH_4Cl;$$

this action is sometimes used to demonstrate the volumetric composition of ammonia.

A glass tube (Fig. 151) is filled with chlorine gas, and strong ammonia from the cup at the top of the tube is allowed to enter in small portions by turning the tap. The action is at first vigorous, each drop of ammonia producing a flash of light. Excess of ammonia is added, and water is then allowed to enter freely from the cup. The water enters until it occupies two-thirds of the tube, the residual gas being nitrogen. Assuming that chlorine, nitrogen, and hydrogen chloride have the formulæ Cl_2, N_2, and HCl, respectively, this action leads to the formula NH_3 for ammonia.

FIG. 151. TUBE FOR DEMONSTRATING THE VOLUMETRIC COMPOSITION OF AMMONIA.

(*d*) *Action of Iodine.*—By the action of iodine, or better of iodine monochloride, on ammonia, a black compound is formed which is generally described as **nitrogen iodide**. After being washed thoroughly with alcohol and then with ether, the product has the composition shown by the formula $N_2H_3I_3$ or NI_3,NH_3 (compare BF_3,NH_3, p. 518). When dry, it explodes under a very slight blow, the products being nitrogen and hydrogen iodide or its elements,

$$N_2H_3I_3 = N_2 + 3HI.$$

(*e*) *Oxidation of Ammonia.*—Both Scheele and Priestley observed that ammonia will burn in oxygen but not in air. The products of combustion are nitrogen and water,

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O;$$

but when red-hot platinum gauze is used as a catalyst,

nitric oxide .to hydriodic acid, *e.g.*, in the refractive power of its
nitric acid (p. 3.

$$4\overset{\cdot}{N}HN_3 \quad + \quad KOH \quad = \quad \underset{\text{Potassium azide}}{KN_3} \quad + \quad H_2O.$$

Nitrogen and water a
heated copper oxide, HI + KOH = $\underset{\text{Potassium iodide}}{KI}$ + H_2O.

$2NH_3$ + 3CuO

but moist ozone oxidises ammo id might be regarded as indicating that
nitrite, nd the hydrogen tervalent. Such an

$4NH_3$ + $7O_3$ = NH_4NO_3 + the generally accepted view that tween two other atoms, and there

Ammonium nitrate can also be proas containing univalent hydrogen
ammonia by air and steam, with platinu of this group are therefore

$$4NH_3 \quad + \quad 4O_2 \quad = \quad 2NH_4NO_3$$

The oxidation of ammonium salts is described la. N·H

(*f*) *Decomposition.*—Ammonia is decomposed
by the action of electric sparks or by heating strongly
the gas is doubled and it becomes insoluble in wat
inflammable; on analysis, it is found to contain 3 O=N(H)(H)(H)
hydrogen to 1 volume of nitrogen (Berthollet, 1785). If
cules of nitrogen and hydrogen are assumed to be diaton the fact
decomposition serves to establish the formula of ammonia as
(compare p. 138).

Gaseous nitrogen is also produced when ammonia is decomposed by chlorine as described above and is a frequent product of the oxidation of ammonium salts.

Detection and Estimation of Ammonia.

Ammonia can be detected qualitatively by its smell and by the formation of a white fume with gaseous hydrogen chloride. Traces of ammonia in solution can be detected and estimated colorimetrically by NESSLER'S REAGENT (p. 884), an alkaline solution of potassium mercury iodide, K_2HgI_4, which gives with ammonia a brown precipitate of the composition NHg_2I,H_2O. Larger quantities of ammonia are estimated by titration against an acid. For this purpose the ammonia may be distilled over into a standard acid and the excess of acid estimated; or the ammonium salt may be boiled with a standard alkali to remove the ammonia and the excess of alkali titrated. A rapid estimation of ammonia may be carried out by adding neutral formaldehyde, CH_2O, to a neutral solution of an ammonium salt; this compound combines with the ammonia as indicated by the equation

$$6CH_2O + 4NH_4Cl = C_6H_{12}N_4 + 6H_2O + 4HCl\,;$$

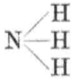
and the acid released can be titrated against a standard alkali, using phenolphthalein as an indicator.

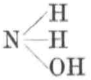
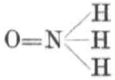
resemblance to hydriodic acid, *e.g.*, in the refractive power of its derivatives :

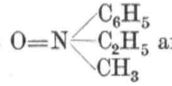
$$HN_3 + KOH = \underset{\text{Potassium azide}}{KN_3} + H_2O.$$

$$HI + KOH = \underset{\text{Potassium iodide}}{KI} + H_2O.$$

The formula of hydrazoic acid might be regarded as indicating that the nitrogen was univalent and the hydrogen tervalent. Such an assumption is quite contrary to the generally accepted view that hydrogen can never act as a link between two other atoms, and there is no difficulty in representing the acid as containing univalent hydrogen and tervalent nitrogen. The compounds of this group are therefore formulated thus :

Ammonia  Hydrazoic acid

Hydrazine Hydroxylamine  or 

The second formula suggested for hydroxylamine is based on the fact that derivatives of the type  are known.

Hydrazoic acid or **azoimide**, HN_3, is prepared by distilling its sodium salt with dilute sulphuric acid.

$$NaN_3 + H_2SO_4 = HN_3 + NaHSO_4.$$

It is a colourless, mobile liquid with a somewhat unpleasant odour ; it boils at 37°, frequently exploding at this temperature, and when frozen melts at — 80°. Its solution is strongly acid and dissolves most of the metals with evolution of hydrogen,

$$2HN_3 + Zn = Zn(N_3)_2 + H_2.$$

The salts are called AZIDES, and many of them are explosive.

Sodium azide, NaN_3, is obtained on passing nitrous oxide over sodamide heated to 190°,

$$2Na{\cdot}NH_2 + N_2O = NaN_3 + NaOH + NH_3,$$

or by mixing *neutral* solutions of sodium nitrite and hydrazine sulphate or nitrate,

$$NaNO_2 + N_2H_4,HNO_3 = NaN_3 + HNO_3 + 2H_2O ;$$

it is the source from which the free acid and its salts are usually derived. Thus **lead azide**, PbN_6, is prepared by precipitating sodium azide with a lead salt, and is used as a substitute for mercury fulminate in detonators.

Hydroxylamine, NH_3O or $NH_2{\cdot}OH$.

Hydroxylamine hydrochloride, $NH_2{\cdot}OH,HCl$, or NH_4OCl, was first prepared by passing nitric oxide through a mixture of tin and hydrochloric acid,

$$2NO + 3Sn + 8HCl = 2NH_4OCl + 3SnCl_2.$$

It can be prepared in a similar manner by the action of tin and hydrochloric acid on nitric acid or on a nitrate or nitrite,

$$NO_2{\cdot}OH + 6H = NH_2{\cdot}OH + 2H_2O.$$

A trace of platinum chloride is added to the mixture to render the tin more active and to promote the evolution of hydrogen at atmospheric temperatures. The tin is removed from solution by means of sulphuretted hydrogen and the filtrate is evaporated to separate the hydroxylamine hydrochloride. The free base can be separated by dissolving the hydrochloride in anhydrous methyl alcohol and adding sodium methoxide, $CH_3{\cdot}ONa$, *i.e.*, methyl alcohol in which sodium has been dissolved :

$$\underset{\text{Hydroxylamine hydrochloride}}{NH_4OCl} + \underset{\text{Sodium methoxide}}{CH_3{\cdot}ONa} = \underset{\text{Hydroxylamine}}{NH_3O} + NaCl + \underset{\text{Methyl alcohol}}{CH_3{\cdot}OH}.$$

The precipitate of sodium chloride is filtered off, the methyl alcohol evaporated under reduced pressure, and the hydroxylamine distilled under a pressure of 20 mm.

Hydroxylamine sulphate, $(NH_4O)_2SO_4$, is prepared commercially by reducing nitrous acid, $NO{\cdot}OH$, to hydroxylamine, $NH_2{\cdot}OH$, namely by passing sulphur dioxide into a concentrated solution of sodium nitrite (2 mols.) and sodium carbonate (1 mol.), cooled to $-3°$, until the solution is slightly acid :

$$2NaNO_2+Na_2CO_3+4SO_2+5H_2O=(NH_4O)_2SO_4+2Na_2SO_4+H_2SO_4+CO_2$$

The solution is kept at 95° for two days, neutralised with sodium carbonate, and concentrated, when sodium sulphate crystallises out on cooling. The hydroxylamine sulphate is obtained by evaporating the mother liquors. The mechanism of this action is explained on p. 388.

Anhydrous **hydroxylamine**, NH_3O, is best prepared by distilling the phosphate in a vacuum,

$$(NH_4O)_3PO_4 = H_3PO_4 + 3NH_2{\cdot}OH.$$

It forms white crystals melting at 33°, and boils at 58° under 22 mm. pressure. It decomposes when heated to 100°. Hydroxylamine is a powerful reducing agent, *e.g.*, it reduces cupric salts to cuprous oxide,

$$\underset{\text{Cupric sulphate}}{4CuSO_4} + 2NH_2OH + 8NaOH = \underset{\text{Cuprous oxide}}{2Cu_2O} + N_2O + 4Na_2SO_4 + 7H_2O\ ;$$

but in alkaline solutions it oxidises ferrous hydroxide to ferric hydroxide,

$$NH_2{\cdot}OH \ + \ 2Fe(OH)_2 \ + \ H_2O \ = \ 2Fe(OH)_3 \ + \ NH_3,$$

and is thereby itself reduced to ammonia.

Sulphonic Derivatives of Ammonia, Hydroxylamine, etc.

The existence of the acid sulphonic group, $—SO_2{\cdot}OH$, has already been indicated in

Sulphuric acid . .	$HO{\cdot}SO_2{\cdot}OH$	Caro's persulphuric acid . . .	$HO{\cdot}O{\cdot}SO_2{\cdot}OH$
Sulphurous acid . .	$H{\cdot}SO_2{\cdot}OH$	Marshall's persulphuric acid .	$O{\cdot}SO_2{\cdot}OH$ | $O{\cdot}SO_2{\cdot}OH$
Chlorosulphonic acid .	$Cl{\cdot}SO_2{\cdot}OH$		
Nitrosulphonic acid	$NO_2{\cdot}SO_2{\cdot}OH$		
Aminosulphonic acid	$NH_2{\cdot}SO_2{\cdot}OH$		
		Pyrosulphuric acid .	$O(SO_2{\cdot}OH)_2$

Inorganic sulphonic acids are also produced by the interaction of sulphites with nitrites; these acids and their salts are important as intermediate stages in the reduction of nitrous acid, *e.g.*, to hydroxylamine, since when the sulphonic acids are hydrolysed by acids the nitrous acid is separated in a reduced form and the sulphurous acid in an oxidised form as sulphuric acid or a sulphate. They therefore provide a mechanism for replacing a hydroxyl group by hydrogen as set out in the following scheme, thus:

$$>N{\cdot}OH \ + \ H{\cdot}SO_2{\cdot}ONa \ \searrow$$
$$>N{\cdot}SO_2{\cdot}ONa \ + \ H_2O.$$
$$>N{\cdot}H \ + \ HO{\cdot}SO_2{\cdot}ONa \ \swarrow$$

Alkaline hydrolysis, on the other hand, usually reproduces the nitrite and sulphite.

The sulphonic derivatives of hydroxylamine are of interest as showing isomerism (p. 321) between the α-compounds, $RO{\cdot}NH_2$, in which the group R (in this case $SO_2{\cdot}OH$) is attached to oxygen, and the β-compounds, $HO{\cdot}NHR$, in which the group R is attached to nitrogen.

(*a*) *Sulphonic Derivatives of Hyponitrous Acid*, HNO or $H_2N_2O_2$.

(i) **Nitrososulphonic acid,** $NO{\cdot}SO_2{\cdot}OH$, formed by replacing the hydroxyl of nitrous acid, $NO{\cdot}OH$, by $-SO_2{\cdot}OH$, has not been isolated, but is assumed by Raschig to be the first product in the lead-chamber process for making sulphuric acid,

$$NO{\cdot}OH \ + \ SO_2 \ = \ NO{\cdot}SO_2{\cdot}OH.$$

It is assumed to be oxidised by nitrous acid to a **nitrosisulphonic acid,** $HO{\cdot}NO{\cdot}SO_2{\cdot}OH$, containing a quadrivalent nitrogen atom, and then decomposed to sulphuric acid and nitric oxide,

$$HO{\cdot}NO \ + \ NO{\cdot}SO_2{\cdot}OH \ = \ HO{\cdot}NO{\cdot}SO_2{\cdot}OH \ + \ NO$$
$$= \ HO{\cdot}SO_2{\cdot}OH \ + \ 2NO.$$

(ii) Direct absorption of nitric oxide by potassium sulphite gives an additive compound,

$$2NO + K_2SO_3 = KO \cdot N{:}N \cdot O \cdot SO_2 \cdot OK,$$

which may be regarded as a monosulphonic-derivative of hyponitrous acid, HON:NOH (see below p. 400).

(b) *Sulphonic Derivatives of Hydroxylamine.*—Replacement of two hydroxyls in orthonitrous acid, $N(OH)_3$, by sulphonic groups gives a **hydroxylamine ββ-disulphonic acid,** $HO \cdot N(SO_3H)_2$, which can be converted into hydroxylamine by hydrolysis,

$$HO \cdot N(SO_3H)_2 + 2H_2O = HO \cdot NH_2 + 2HO \cdot SO_2 \cdot OH.$$

The **sodium salt** is an intermediate product in the preparation of hydroxylamine from sodium nitrite, sodium carbonate, and sulphur dioxide (p. 386). The corresponding **potassium hydroxylamine ββ-disulphonate,** $HO \cdot N(SO_3K)_2, 2H_2O$, is prepared more readily from KNO_2 and $K_2S_2O_5$ at 0°,

$$2KNO_2 + 3K_2S_2O_5 + H_2O = 2HO \cdot N(SO_3K)_2 + 2K_2SO_3,$$

and is the most convenient starting-point for a series of other derivatives. Thus by oxidation with silver oxide or lead peroxide in alkaline solution it yields first a violet **nitrosodisulphonate,** $O{:}N(SO_3K)_2$, or perhaps

$$\begin{array}{l} O{=}N(SO_3K)_2 \\ \quad\;\; | \\ O{=}N(SO_3K)_2 \end{array},$$

and then a **potassium hydroxylamine αββ-trisulphonate,**

$$KO \cdot SO_2 \cdot O \cdot N(SO_3K)_2, H_2O,$$

$$2PbO_2 + 3HO \cdot N(SO_3K)_2 + KOH = 2Pb(OH)_2 + 2NO(SO_3K)_3 + KNO_2.$$

By partial hydrolysis of the disulphonate, a **potassium hydroxylamine β-monosulphonate,** $HO \cdot NH \cdot SO_3K$, is produced, whilst complete hydrolysis gives hydroxylamine sulphate, $HO \cdot NH_2, H_2SO_4$.

By partial hydrolysis of the trisulphonate a **potassium hydroxylamine αβ-disulphonate,** $KO \cdot SO_2 \cdot O \cdot NH \cdot SO_2 \cdot OK$, is produced, isomeric with the ββ-disulphonate described above, from which it differs in crystallising in an anhydrous condition and in giving no coloration with lead peroxide, whilst its stability at 100° distinguishes it from the trisulphonate from which it is derived. In acid solutions the αβ-disulphonic acid oxidises potassium iodide and is reduced to ammonia,

$$NH\left\langle\begin{array}{l} SO_3H \\ O \cdot SO_3H \end{array}\right. + 2HI + H_2O = NH_3 + 2H_2SO_4 + I_2,$$

probably as a result of a partial hydrolysis to **hydroxylamine α-monosulphonic acid,** $NH_2 \cdot O \cdot SO_2 \cdot OH$ (compare Caro's persulphuric acid, $HO \cdot O \cdot SO_2 \cdot OH$); this unstable acid is isomeric with the **hydroxylamine β-monosulphonic acid,** $HO \cdot NH \cdot SO_2 \cdot OH$, of which the potassium salt has already been mentioned, and which is sufficiently stable to be prepared in the form of a syrup (compare aminosulphonic acid, $NH_2 \cdot SO_2 \cdot OH$).

(c) *Sulphonic Derivatives of Ammonia.*—Replacement of three hydroxyls in orthonitrous acid, $N(OH)_3$, gives the trisulphonic acid, $N(SO_3H)_3$, which on complete hydrolysis would yield ammonia, NH_3, but usually breaks down only to the very stable aminosulphonic acid, $NH_2 \cdot SO_2 \cdot OH$. **Potassium**

aminotrisulphonate, $N(SO_3K)_3,2H_2O$, is prepared from potassium nitrite and an excess of potassium metabisulphite,

$$KNO_2 + 2K_2S_2O_5 = N(SO_3K)_3 + K_2SO_3.$$

It can be recrystallised from alkaline solution, but when boiled with water splits off two-thirds of its sulphur as sulphate, whilst the remaining one-third is retained in the form of an aminosulphonate, $NH_2{\cdot}SO_2{\cdot}OK$, which is not precipitated by barium chloride.

Potassium iminodisulphonate, $NH(SO_3K)_2$, the first product of hydrolysis of the preceding compound, is of interest because the hydrogen of the bivalent IMINO-GROUP, $>NH$, as well as of the sulphonic group, can be replaced by metals. Thus ammonia forms salts of two types, namely, **ammonium iminodisulphonate,** $NH(SO_3NH_4)_2$, and **basic ammonium iminodisulphonate,** $NH_4{\cdot}N(SO_3NH_4)_2$; these have been known since 1834 as additive products of ammonia and sulphur trioxide:

$$3NH_3 + 2SO_3 = NH(SO_3NH_4)_2$$
$$4NH_3 + 2SO_3 = NH_4{\cdot}N(SO_3NH_4)_2.$$

The free acid, **iminodisulphonic acid,** $NH(SO_3H)_2$, is also known.

Potassium aminosulphonate, $NH_2{\cdot}SO_2{\cdot}OK$, is the potassium salt of **aminosulphonic acid,** $NH_2{\cdot}SO_2{\cdot}OH$, a stable, crystalline acid decomposing at 205°, and is the final product of the hydrolysis by boiling water of the preceding salts.

(*d*) *Sulphonic Derivatives of the Cyanides.*—Hydrogen cyanide (as potassium cyanide) unites with two molecular proportions of potassium hydrogen sulphite to form **potassium aminomethane disulphonate,**

$$HCN + 2KHSO_3 = H_2N{\cdot}CH(SO_3K)_2.$$

This compound is of interest, since with nitrous acid it gives a **potassium diazomethane disulphonate,** $\begin{matrix}N\\\|\\N\end{matrix}\!>C(SO_3K)_2,H_2O$, which loses nitrogen in forming additive compounds, *e.g.*, with hydrogen iodide it gives $CHI(SO_3K)_2,2H_2O$, and with iodine $CI_2(SO_3K)_2$.

NITROGEN AND OXYGEN.

Oxides and Oxy-acids of Nitrogen.

Nitrogen forms the following series of oxides and oxy-acids:

Hyponitrous acid .	$(HNO)_2$	Nitrous oxide .	N_2O
		Nitric oxide .	NO
Nitrous acid . .	HNO_2	Nitrous anhydride	N_2O_3
		Nitrogen peroxide	NO_2 or N_2O_4
Nitric acid . . .	HNO_3	Nitric anhydride .	N_2O_5

There is also a pernitric compound of uncertain composition, perhaps NO_3 or N_2O_7.

All these compounds were first prepared from saltpetre or nitre, KNO_3, and nitrogen itself derives its name from the fact that when

sparked with oxygen over potash it converts the potassium hydroxide into nitre :

$$2N_2 + 5O_2 + 4KOH = 4KNO_3 + 2H_2O.$$

Preparation of Nitric Acid.

(*a*) *From Chile Saltpetre.*—Nitric acid is prepared by the action of sulphuric acid on Chile saltpetre,

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$

The mixture is distilled in cast-iron pots, connected to condensers made of fused silica or of acid-resisting earthenware (Fig. 152). The greater part of the nitric acid is of 90 to 95 per cent. strength, but in the final stages of the action, when the sulphuric acid is becoming exhausted, a weaker acid (40 to 65 per cent. HNO_3) distils. Provision is also made for the oxidation and absorption in water as dilute nitric acid of gaseous oxides of nitrogen set free by the decomposition of the acid, *e.g.*,

$$4NO + 3O_2 + 2H_2O = 4HNO_3.$$

The residue of NITRE-CAKE consists mainly of the acid compound, sodium hydrogen sulphate or sodium bisulphate, $NaHSO_4$, and not (as in the preparation of muriatic acid from salt) of the neutral sulphate, Na_2SO_4, since at the temperature required to displace completely the second hydrogen atom of the sulphuric acid a very extensive decomposition of nitric acid takes place ; it is also important to use sufficient acid to produce a nitre-cake which can be withdrawn from the nitre-pots as a fluid.

(*b*) *From Ammonia.*—Ammonia is oxidised to nitric oxide by passing a mixture of ammonia and air over red-hot platinum gauze (Ostwald process),

$$4NH_3 + 5O_2 = 4NO + 6H_2O.$$

The mixture used contains about 8 per cent. of ammonia ; if richer mixtures are used there is a serious loss by oxidation to nitrogen,

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O.$$

The nitric oxide is oxidised by air and absorbed in water,

$$4NO + 3O_2 + 2H_2O = 4HNO_3.$$

(*c*) *From Air.*—Nitric oxide (p. 404) is produced by the action of the electric arc on air,

$$N_2 + O_2 = 2NO.$$

The nitric oxide is oxidised and absorbed in water as in (*a*) and (*b*).

(*d*) *Absorption of Nitric Oxide.*—The absorption of nitric oxide in (*b*) and (*c*) is effected on the COUNTER-CURRENT SYSTEM by passing the gases in an upward direction through a series of from 5 to 7 towers packed with quartz, in which the oxides of nitrogen are washed out by a downward flow of acids of progressively diminishing strength, whilst the acid, which is worked gradually in the opposite direction

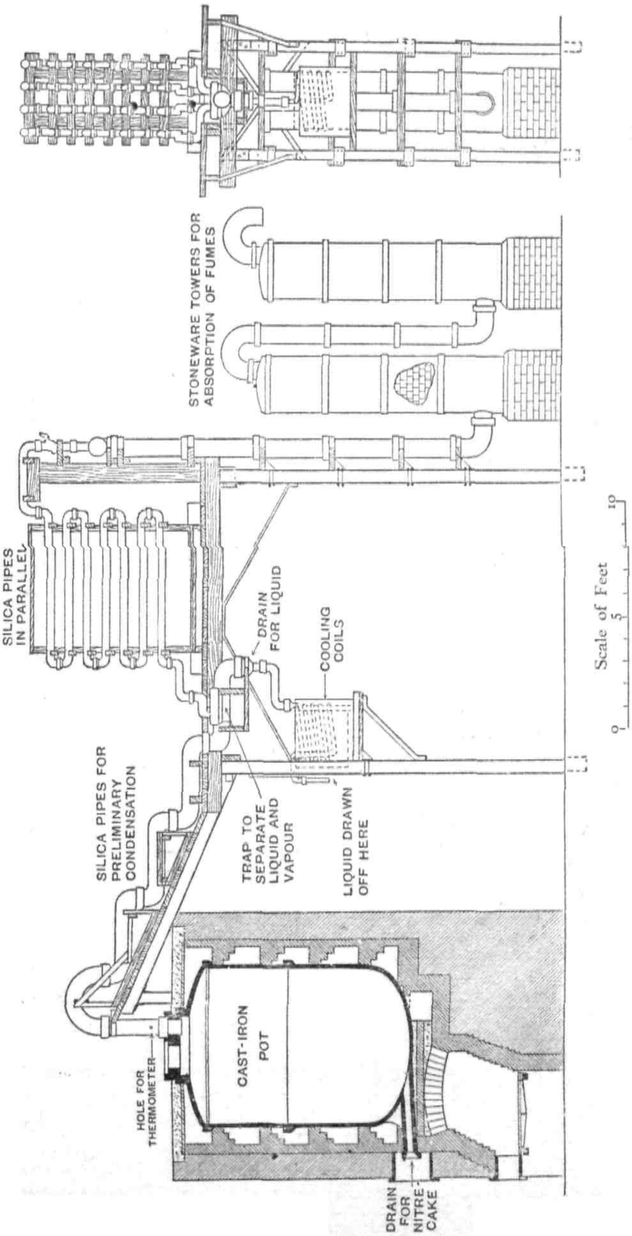


FIG. 152.—PLANT FOR MANUFACTURE OF NITRIC ACID.

from tower to tower, increases progressively in strength by absorption of nitric acid from the gases. In two typical cases the strengths of the acids in the towers were as follows :

Oxidation of Ammonia.		*Oxidation of Nitrogen.*	
Seventh tower .	3% HNO_3	Fourth tower . .	0—5%
Third ,, .	34% HNO_3	Third ,, . .	5—15%
Second ,, .	42% HNO_3	Second ,, . .	15—25%
First ,, .	47% HNO_3	First ,, . .	25—50%

In the former case only a part of the acid was passed forward from tower to tower, the major portion being kept in circulation in the same tower. In the latter case the acid flowed only once down each tower.

(*e*) *Concentration of Nitric Acid.*—The dilute nitric acid prepared as in (*d*) can be concentrated by mixing it with two or three times its own weight of 92 per cent. sulphuric acid and allowing the mixture to flow down a tower packed with quartz. The heat set free on mixing the two acids causes strong nitric acid (about 98 per cent. HNO_3) to distil from the top of the tower, and steam is passed into the bottom to remove the last traces of nitric acid from the sulphuric acid before sending it to be concentrated again for further use.

In the laboratory, anhydrous nitric acid can be prepared by distilling with sulphuric acid the commercial "fuming" nitric acid of density 1·52.

Physical Properties of Nitric Acid.

When free from water and from oxides of nitrogen, nitric acid is a colourless liquid having a density of 1·52 at 15°. It boils with partial decomposition at 86° and freezes to a snow-white solid at − 41°.

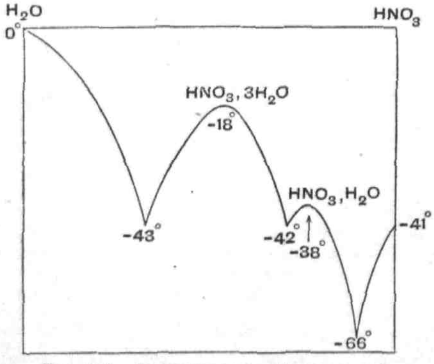


FIG. 153.—FREEZING-POINT DIAGRAM FOR NITRIC ACID AND WATER.

Nitric acid combines with water to form a **monohydrate**, HNO_3,H_2O (77·75% HNO_3), freezing at − 38°, and a **trihydrate,** $HNO_3,3H_2O$ (53·8% HNO_3), freezing at − 18°. (Fig. 153.)

When dilute nitric acid is distilled the boiling-point rises gradually to 121°, at which temperature an acid containing 68 per cent. of nitric acid, HNO_3, distils ; this is the ordinary commercial acid of density 1·414. When a stronger acid is distilled it loses nitric acid until its concentration has fallen to 68 per cent., when the mixture of constant boiling-point again distils.

Chemical Properties of Nitric Acid.

(*a*) *Acid Properties.*—Pure nitric acid is without action on the metals and does not even act upon chalk. When water is added, it develops the characteristics of a monobasic acid, and forms a series of NITRATES, of which **sodium nitrate**, $NaNO_3$, is important as the principal source of nitric acid, **potassium nitrate**, KNO_3, as a constituent of gunpowder, **ammonium nitrate**, NH_4NO_3, as a constituent of military and commercial explosives, **silver nitrate**, $AgNO_3$, as a caustic and as the principal soluble salt of silver, and **lead nitrate**, $Pb(NO_3)_2$, as the principal soluble salt of lead. These can be prepared in a normal manner by the action of nitric acid on the corresponding oxides or carbonates, but when nitrates are prepared directly from the metals, reduction of the acid takes place (see below) and considerable loss of acid occurs. Thus, it is much more economical to prepare lead nitrate from lead oxide (*e.g.*, from the lead oxide obtained as a by-product in the preparation of nitrites, p. 396) than to make it from metallic lead.

(*b*) *Decomposition.*—When nitric acid is heated it decomposes according to the equation

$$4HNO_3 = O_2 + 4NO_2 + 2H_2O.$$

The formation of oxygen as a decomposition product of nitric acid may be shown readily by allowing nitric acid to drip slowly through a red-hot clay pipe and collecting the oxygen over water in the usual way (Fig. 154). It is probable that the acid is first decomposed into water and nitric anhydride,

$$2HNO_3 = H_2O + N_2O_5,$$

and that the nitric anhydride is then decomposed according to the equation

$$2N_2O_5 = 4NO_2 + O_2;$$

the decomposition is therefore brought about most readily in strong nitric acid. Decomposition is also promoted by exposure to light, and the oxygen liberated from strong nitric acid in sunlight may produce enough pressure to burst the bottle in which the acid is contained.

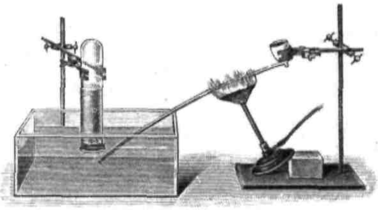


FIG. 154.—DECOMPOSITION OF NITRIC ACID BY HEAT.

(*c*) *Nitric Acid as an Oxidising Agent.*—The ready liberation of oxygen from nitric acid makes it a powerful oxidising agent, especially when concentrated.

(i) Nitric acid will liberate sulphur from sulphuretted hydrogen and iodine from potassium iodide.

$$3H_2S + 2HNO_3 = 3S + 2NO + 4H_2O.$$
$$6KI + 8HNO_3 = 3I_2 + 6KNO_3 + 4H_2O + 2NO.$$

(ii) It liberates chlorine from hydrochloric acid, *e.g.*, in aqua regia,

$$3HCl + HNO_3 = Cl_2 + \underset{\text{Nitrosyl chloride}}{NOCl} + 2H_2O.$$

and enables this to dissolve gold as shown in the equation

$$4HCl + HNO_3 + Au = HAuCl_4 + NO + 2H_2O.$$

(iii) Hot nitric acid will oxidise sulphur to sulphuric acid, either alone, or in the presence of barium nitrate, *e.g.*, when it is desired to estimate the sulphur as barium sulphate,

$$S + 2HNO_3 = H_2SO_4 + 2NO,$$
$$S + Ba(NO_3)_2 = BaSO_4 + 2NO.$$

(iv) In qualitative analysis nitric acid is used to oxidise ferrous to ferric salts, *e.g.*,

$$6FeCl_2 + 6HCl + 2HNO_3 = 6FeCl_3 + 4H_2O + 2NO.$$

(v) The reduction of nitric acid to nitrous acid, hydroxylamine, ammonia, etc., as described above under these headings, may all be regarded as illustrations of the oxidising properties of nitric acid.

(vi) It will oxidise many organic compounds, *e.g.*, sugar to oxalic acid.

(*d*) *Action of Nitric Acid on the Metals.*—In its action on metals nitric acid plays a double part, (i) as an acid, (ii) as an oxidising agent; it is therefore able to dissolve copper, mercury, and silver, which are usually insoluble in dilute acids, although it will not dissolve gold and platinum, which are, however, soluble in chlorinating acids.

When metals are dissolved in nitric acid, a large number of reduction-products are formed, by parallel reactions which cannot be covered by a single equation.

(i) In the case of *copper*, the formation of nitric oxide may be shown by the equation

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O,$$

but higher and lower oxides may also be formed. The action appears to take place only in the presence of oxides of nitrogen, which are perhaps the active substances in the attack upon the metal, and the action can be held up almost entirely by removing these oxides from nitric acid of 30 per cent. strength.

(ii) Similar equations may be given for the action of nitric acid on *silver*, *mercury*, and *lead*.

(iii) In the case of *tin*, strong nitric acid acts mainly as an oxidising agent, converting the tin into metastannic acid, $(H_2SnO_3)_n$, a hydrated form of the oxide SnO_2.

(iv) In the case of *zinc* and other easily oxidised metals, lower oxides of nitrogen, such as nitrous oxide, N_2O, and nitrogen

gas may be formed, in addition to nitric oxide; in alkaline solutions reduction to ammonia takes place, *e.g.*,

$$\underset{\text{}}{NaNO_3} + 4Zn + 7NaOH = NH_3 + \underset{\text{Sodium zincate}}{4Na_2ZnO_2} + 2H_2O.$$

(v) *Nitric acid will not dissolve aluminium, although this metal* is readily attacked by dilute hydrochloric acid; strong nitric acid also has the curious property of rendering iron PASSIVE, that is, of bringing the surface into an inactive condition in which it is not attacked even by dilute nitric acid. These actions are only imperfectly understood, but have been attributed to the production of insoluble films of oxide on the surface of the metal.

(*e*) *Nitration.*—Nitric acid is used extensively in organic chemistry to effect NITRATION, *i.e.*, to replace hydrogen by the NITRO-GROUP, $-NO_2$. This process is usually effected by the action of a mixture of nitric and sulphuric acids, the latter acid serving to remove the water formed in the action, and apparently diminishing also the tendency of the nitric acid to act as an oxidising agent. Three typical actions, in each of which three hydrogen atoms are replaced by three nitro-groups, are shown in the equations

$$\underset{\text{Glycerine}}{C_3H_8O_3} + 3HNO_3 = \underset{\text{Nitroglycerine}}{C_3H_5(ONO_2)_3} + 3H_2O;$$

$$\underset{\text{Toluene}}{C_6H_5{\cdot}CH_3} + 3HNO_3 = \underset{\text{Trinitrotoluene}}{CH_3{\cdot}C_6H_2(NO_2)_3} + 3H_2O;$$

$$\underset{\text{Phenol}}{C_6H_5{\cdot}OH} + 3HNO_3 = \underset{\text{Picric acid}}{HO{\cdot}C_6H_2(NO_2)_3} + 3H_2O.$$

These three compounds are all very powerful explosives, the oxygen of the nitro-groups oxidising the carbon and hydrogen of the organic nucleus with very great rapidity and great evolution of heat when the compound is detonated, *e.g.*, by a sudden blow, delivered either mechanically or by some other more sensitive explosive.

Detection of Nitric Acid.

A nitrate may be detected by the following reactions:—

(i) On ignition, brown fumes of nitrogen dioxide are evolved, except from sodium, potassium, and ammonium nitrates, *e.g.*,

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

(ii) Nitric acid is set free on heating with strong sulphuric acid, and brown fumes of the dioxide are evolved at the same time owing to the partial decomposition of the nitric acid.

(iii) Ferrous sulphate and sulphuric acid produce a brown colour which is discharged on warming (p. 406); nitrites give the same coloration with ferrous sulphate and acetic acid.

(iv) Sulphuric acid with a trace of brucine gives a pink colour.
(v) Sulphuric acid and diphenylamine produce a blue colour even with minute traces of nitric acid.

Estimation of Nitric Acid and Nitrates.

(i) Pure nitric acid may be estimated by direct titration with standard alkali.
(ii) Small quantities of nitrates may be estimated by a colorimetric process. The solution is heated with phenolsulphonic acid and sulphuric acid, and ammonia is added to the product. The yellow colour of the ammonium picrate thus formed is compared with standard tints in "Nessler glasses" (compare p. 383).

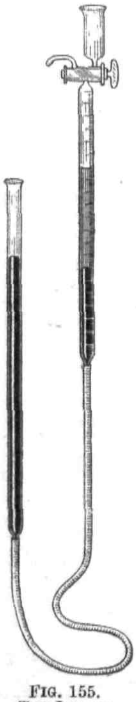


FIG. 155. THE LUNGE NITROMETER.

(iii) Larger quantities of nitrates are estimated by shaking with mercury and sulphuric acid (about 94% H_2SO_4 is best) in the LUNGE NITROMETER (Fig. 155), when the nitric acid is reduced quantitatively to nitric oxide,

$$6Hg + 2HNO_3 + 3H_2SO_4 = 3Hg_2SO_4 + 2NO + 4H_2O.$$

The volume of nitric oxide is measured and used to calculate the proportion of nitrogen in the original material.
(iv) The nitrate may be reduced to nitric oxide by the action of ferrous chloride and hydrochloric acid,

$$3FeCl_2 + HNO_3 + 3HCl = 3FeCl_3 + NO + 2H_2O,$$

and the nitric oxide boiled out and collected over water (Fig. 156) (Schultze-Tiemann method).
(v) The nitrate may be reduced to ammonia by means of a zinc-copper couple (*i.e.*, zinc rendered specially active by coating it with finely-divided copper by immersion in a solution of copper sulphate) or of zinc and iron dust in presence of an alkali, and the ammonia estimated colorimetrically or by titration.

Nitrous Acid, HNO_2.

When potassium nitrate is heated either alone or with metallic lead, it loses an atom of oxygen and is converted into potassium nitrite,

$$KNO_3 + Pb = KNO_2 + PbO.$$

The removal of this atom of oxygen alters completely the properties of the parent acid. Nitric acid is one of the strongest acids, comparing well with hydrochloric acid, and is considerably stronger than an

equivalent quantity of sulphuric acid; nitrous acid, on the other hand, is a very weak acid which can be displaced from its salts, not only by mineral acids, but also by weak vegetable acids, such as acetic acid. The acid is also extremely unstable, breaking down at once into water and nitrous anhydride, which in its turn decomposes into nitric oxide and nitrogen peroxide:

$$\underset{\text{Nitrous acid}}{2HNO_2} = H_2O + \underset{\text{Nitrous anhydride}}{N_2O_3} = H_2O + \underset{\text{Nitric oxide}}{NO} + \underset{\text{Nitrogen peroxide}}{NO_2}.$$

On adding an acid to potassium nitrite, therefore, vigorous effervescence takes place and brown fumes are liberated which contain both nitric oxide and nitrogen peroxide.

Nitrous acid has never been isolated, but there is no doubt as to its existence in aqueous solutions at low temperatures. Thus, alcoholic solutions of potassium nitrite and hydrochloric acid, cooled by means of carbon dioxide snow, can be mixed without effervescence; and even at the ordinary temperature mixtures of a nitrite with an acid can be used to produce chemical changes which can only be attributed to the action of nitrous acid—*e.g.*, nitrous acid will convert aniline, $C_6H_5{\cdot}NH_2$, into "diazobenzene hydroxide," $C_6H_5{\cdot}N_2{\cdot}OH$, by eliminating two atoms of hydrogen from the base and an atom of oxygen from the acid,

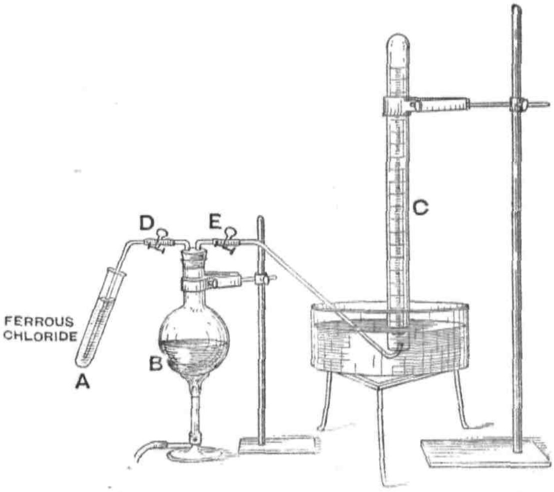


FIG. 156.—SCHULTZE-TIEMANN APPARATUS FOR ESTIMATION OF NITROGEN IN NITRATES, ETC.

The liquid *B* containing the material to be tested is boiled till free from air. A solution of ferrous chloride in hydrochloric acid is drawn in by closing the clip *E* and opening the clip *D* after removing the burner. The liquid *B* is again boiled and the nitric oxide released through the clip *E* is collected and measured in *C*.

$$C_6H_5{\cdot}N\boxed{H_2 + O}{:}NOH = H_2O + C_6H_5{\cdot}N{:}N{\cdot}OH.$$

By mixing an excess of hydrochloric acid with the aniline, this action can be used to estimate either aniline or nitrous acid, paper dipped in a solution of potassium iodide and starch being used as an indicator to show when an excess of nitrous acid has been added to the aniline.

Nitrous acid is a more powerful oxidising agent than nitric acid, but this is perhaps due in part to the readiness with which it decomposes. Thus, although nitrous acid liberates iodine from potassium iodide, this action is also brought about by nitrogen peroxide, and it is difficult to say which of these two substances is the actual oxidising agent.

Detection of Nitrous Acid.

(i) On adding dilute sulphuric acid, potassium iodide, and a solution of starch to a nitrite, a blue colour develops, by liberation of iodine which combines with the starch. Nitrates produce a similar colour only after standing for some time.

(ii) Ferrous sulphate and acetic acid produce a brown colour which is discharged on warming, brown fumes being evolved (compare detection of nitric acid, p. 395).

(iii) Meta-phenylenediamine in acid solutions gives a brown colour with nitrous acid.

Estimation of Nitrous Acid and Nitrites.

(i) Nitrites can be estimated by reduction to nitric oxide as in the case of nitric acid.

(ii) When present in smaller quantities, the nitrite may be reduced to ammonia by means of a zinc-copper couple and the ammonia estimated by Nessler's solution or by titration as in the case of nitric acid.

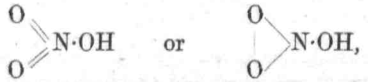
(iii) In the absence of other oxidisable compounds, nitrous acid (*e.g.*, in "waste acids" from nitration) can be estimated by oxidation with potassium permanganate,

$$2KMnO_4 + 3H_2SO_4 + 5HNO_2 = K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O.$$

(iv) Traces of nitrites may be estimated by means of the colour produced with meta-phenylenediamine.

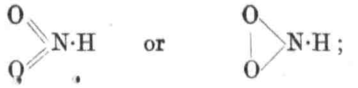
Constitution of Nitric and Nitrous Acids.

Nitric acid is universally regarded as formed by the union of a nitro-group, NO_2, with a hydroxyl group, OH, as shown in the formula $NO_2 \cdot OH$. There is, however, some doubt as to the structure of the nitro-group, and the formula of the acid may be written



the nitrogen atom being quinquevalent in the first formula and tervalent in the second.

Nitrous acid is probably O:N·OH, but compounds are known which are derived from the formula $NO_2·H$, *i.e.*,



these must therefore also be regarded as possible formulæ for the acid.

Nitrosyl and Nitroxyl Compounds.

The formulæ for nitrous and nitric acids receive support from the production of analogous compounds in which the hydroxyl group has been displaced by a halogen atom.

(*a*) **Nitrosyl fluoride**, NOF, or O:N·F (compare nitrous acid, O:N·OH), is prepared by the action of nitrosyl chloride on silver fluoride,

$$NOCl + AgF = NOF + AgCl.$$

It is a gas which condenses to a liquid boiling at − 56° and freezing at − 134°. It is decomposed by water, giving nitrous and hydrofluoric acids. Silicon, boron, red phosphorus, and sodium take fire in the gas and burn to fluorides, liberating nitric oxide ; and arsenic and antimony are attacked in a similar manner, but without burning.

(*b*) **Nitroxyl fluoride**, NO_2F (compare nitric acid, $NO_2·OH$) was prepared by Moissan by the action of fluorine on nitric oxide at the temperature of liquid oxygen,

$$4NO + F_2 = 2NO_2F + N_2.$$

It is a colourless gas, which condenses to a liquid boiling at − 63·5°, and when frozen melts at − 139°. It is decomposed by cold water, yielding nitric and hydrofluoric acids,

$$NO_2F + H_2O = NO_2·OH + HF.$$

It has no action on hydrogen, sulphur, or carbon, but acts like nitrosyl fluoride in converting silicon, boron, phosphorus, and many metals into fluorides.

(*c*) **Nitrosyl chloride**, NOCl, can be prepared

(i) By the action of phosphorus pentachloride on a nitrite,

$$KNO_2 + PCl_5 = NOCl + KCl + POCl_3.$$

This is the normal method of replacing hydroxyl by chlorine.

(ii) By the direct combination of nitric oxide and chlorine in presence of charcoal at 50° (compare the preparation of carbonyl chloride or phosgene, $COCl_2$, p. 453),

$$2NO + Cl_2 = 2NOCl.$$

(iii) By the action of chamber crystals (nitrosulphonic acid or nitrosyl sulphate) on sodium chloride.

$$\underset{\text{Nitrosyl sulphate (chamber crystals)}}{ON·O·SO_2·OH} + NaCl = \underset{\text{Nitrosyl chloride}}{ON·Cl} + \underset{\text{Sodium bisulphate}}{NaO·SO_2·OH}.$$

Nitrosyl chloride is a yellow gas which condenses to a red liquid boiling at $-5°$. It freezes to a yellow solid, melting at $-60°$. It forms additive compounds with some metallic chlorides, *e.g.*, $BiCl_3,NOCl$ and $SnCl_4,2NOCl$, and with organic compounds such as pinene, the principal constituent of turpentine,

$$\underset{\text{Pinene}}{C_{10}H_{16}} + NOCl = \underset{\text{Pinene nitrosochloride}}{C_{10}H_{16},NOCl.}$$

Like other acid chlorides, nitrosyl chloride is decomposed by alkalies, and by basic oxides, giving a chloride and a salt of the original acid,

$$NOCl + 2KOH = KNO_2 + KCl + H_2O.$$

(*d*) **Nitroxyl chloride,** NO_2Cl, the chloride of nitric acid, $NO_2{\cdot}OH$, has been described as a product of the action of chlorine on silver nitrite,

$$AgNO_2 + Cl_2 = AgCl + NO_2Cl.$$

The liquid product boils at 5°, but has not been isolated in the crystalline form; it is perhaps in part a mixture of liquid nitrogen peroxide and liquid chlorine,

$$2NO_2Cl \rightleftharpoons N_2O_4 + Cl_2.$$

(*e*) **Nitrosyl bromide**, NOBr, and **nitrosyl tribromide**, $NOBr_3$ (compare $POCl_3$ and $POBr_3$), are formed by direct combination of nitric oxide with bromine.

Hyponitrous Acid, $(HNO)_2$.

(*a*) *Preparation.*—The nitrites can be reduced to HYPONITRITES by the action of sodium amalgam as represented by the equation:

$$\underset{\text{Potassium nitrite}}{KNO_2} + 2NaHg_2 + H_2O = \underset{\text{Potassium hyponitrite}}{KNO} + 2NaOH + 4Hg.$$

After reduction, the solution is neutralised with acetic acid, and silver nitrate is added, when a yellow precipitate of **silver hyponitrite**, AgNO or $Ag_2N_2O_2$, is thrown down. **Hyponitrous acid**, $H_2N_2O_2$, can be prepared from this salt by the action of hydrogen chloride in presence of ether, and **ammonium hyponitrite**, $(NH_4)HN_2O_2$, can be precipitated by passing dry ammonia gas into the ethereal solution of the acid.

(*b*) *Properties.*—The acid separates from its ethereal solution in flat crystals which explode spontaneously when dry. In aqueous solutions, the acid decomposes slowly, liberating nitrous oxide,

$$H_2N_2O_2 = H_2O + N_2O.$$

It is readily oxidised to nitric acid either by bromine or by neutral potassium permanganate.

An isomer of hyponitrous acid, known as **nitroamide**, $H_2N{\cdot}NO_2$, is known, but has not been prepared by any simple method.

(*c*) *Constitution.*—The constitution of hyponitrous acid is shown by its preparation from hydroxylamine sulphate and potassium nitrite

in the presence of lime or chalk. In this action nitrous acid interacts with hydroxylamine in precisely the same way as with aniline; hyponitrous acid is therefore a "diazo-compound" containing the group —N=N—, formed by elimination of a molecule of water as shown in the equation

$$\underset{\text{Hydroxylamine}}{HO{\cdot}N\,H_2} + \underset{\text{Nitrous acid}}{O\,NOH} = \underset{\text{Hyponitrous acid}}{HO{\cdot}N{:}N{\cdot}OH} + H_2O.$$

The molecular formula, $H_2N_2O_2$, is confirmed by the freezing-point of the acid in aqueous solutions, and by the vapour density of its diethyl derivative, $(C_2H_5)_2N_2O_2$.

Oxides of Nitrogen.

The seven oxides of nitrogen may be grouped into two series according as they contain one or two atoms of nitrogen.

N_1 *Series.*		N_2 *Series.*	
		N_2O_6(?)	Pernitric anhydride.
		N_2O_5	Dinitrogen pentoxide or nitric anhydride.
NO_2	Nitrogen dioxide.	N_2O_4	Dinitrogen tetroxide.
		N_2O_3	Dinitrogen trioxide or nitrous anhydride.
NO	Nitric oxide (or nitrogen monoxide)*	N_2O_2	is not known.
		N_2O	Dinitrogen monoxide or nitrous oxide.

(*a*) Two of these oxides are anhydrides of known acids, namely, **nitric anhydride**, N_2O_5, and **nitrous anhydride**, N_2O_3; **dinitrogen tetroxide**, N_2O_4, may also be regarded as a mixed anhydride of these two acids. A fourth oxide, **nitrous oxide**, N_2O, can be produced by loss of water, from hyponitrous acid, but is not called hyponitrous anhydride, because the oxide is entirely devoid of acid properties and does not give hyponitrous acid when dissolved in water.

(*b*) **Nitrogen dioxide**, NO_2, and **dinitrogen tetroxide**, N_2O_4, are very readily convertible into one another, and the name **nitrogen peroxide** is used to describe the substance when it is not desired to specify in which of the two forms it is present, or to describe a gas or liquid in which both oxides are present in equilibrium with one another as shown in the equation

$$N_2O_4 \rightleftharpoons 2NO_2.$$

Nitrogen dioxide, NO_2, is brown, whilst dinitrogen tetroxide is colourless. Nitrous anhydride, N_2O_3, is blue, but is very unstable and can only

* This name is sometimes applied loosely to dinitrogen monoxide, N_2O, and is therefore too ambiguous to be used safely.

be obtained at low temperatures. When the *blue* anhydride is mixed with the *brown* dioxide, which is one of its products of decomposition, a *green* liquid may be produced, but all the other oxides and acids of nitrogen are colourless.

(*c*) **Nitric oxide**, NO, the simplest and most stable compound of nitrogen and oxygen, was one of the first two gases to be prepared artificially and collected over water (Mayow, 1674). It is the only oxide of nitrogen that does not dissolve readily in cold water, and is therefore obtained as the chief gaseous product of reduction of nitric acid by metals, when the gases are collected over water. It will be convenient to describe this oxide first, followed by the two gases, N_2O and NO_2, which are formed from it by reduction and oxidation, and to describe last the more complex oxides of the N_2 series.

Thermochemistry of the Oxides of Nitrogen.

The oxides of nitrogen are for the most part endothermic compounds, the heats of formation being as follows:

Nitrous oxide, N_2O	— 20,600 calories.
Nitric oxide, NO	— 21,600 calories.
Nitrogen dioxide, NO_2	— 4,000 calories (about).

The heat of formation of N_2O_4 is not known very accurately, but is almost zero, whilst that of N_2O_5 is given as — 1200 calories. Nitric acid, HNO_3, is an exothermic compound with a heat of formation from its elements of 41,600 calories, but its heat of formation from water, nitrogen, and oxygen is only $41{,}600 - \frac{1}{2} \times 68{,}360 = 7420$ cal.

The stability of these compounds appears to be determined, however, much more by the size of the molecules than by their heats of formation. Thus, nitric oxide, which is the most endothermic compound of the series but has the smallest molecule, is by far the most stable, since it does not begin to decompose below 1000°. On the other hand, nitrogen dioxide, NO_2, with a negative heat of formation of only — 4000 calories, is decomposed completely into nitric oxide and oxygen at 800°; and dinitrogen tetroxide, N_2O_4, which may be almost an exothermic compound, is decomposed completely into the endothermic nitrogen dioxide, NO_2, at 150°. Strong nitric acid, with a positive heat of formation of + 41,600 calories, is also decomposed readily either by heat or by exposure to light.

Preparation of Nitric Oxide, NO.

(*a*) *By Reduction of Nitric Acid.*

(i) Mayow obtained nitric oxide by the action of iron on dilute nitric acid. It is more conveniently prepared by the action of copper on the acid (Fig. 157) as shown in the equation

$$3Cu + 8HNO_3 = \underset{\text{Cupric nitrate}}{3Cu(NO_3)_2} + \underset{\text{Nitric oxide}}{2NO} + 4H_2O.$$

(ii) By the action of mercury and concentrated sulphuric acid (as in the Lunge nitrometer, p. 396) nitric acid is reduced quantitatively to nitric oxide as shown in the equation

$$6Hg + 2HNO_3 + 3H_2SO_4 = 3Hg_2SO_4 + 2NO + 4H_2O.$$

(iii) Pure nitric oxide can be prepared by reducing nitric acid with ferrous sulphate,

$$2KNO_3 + 6FeSO_4 + 4H_2SO_4 = 2NO + 3Fe_2(SO_4)_3 + K_2SO_4 + 4H_2O$$

Cold concentrated sulphuric acid is mixed with powdered potassium nitrate and a saturated solution of ferrous sulphate is poured upon the mixture; this solution forms a separate layer on the top of the acid, and a black ring develops between the two liquids (p. 406). When the two layers are mixed together, heat is evolved and gaseous nitric oxide set free.

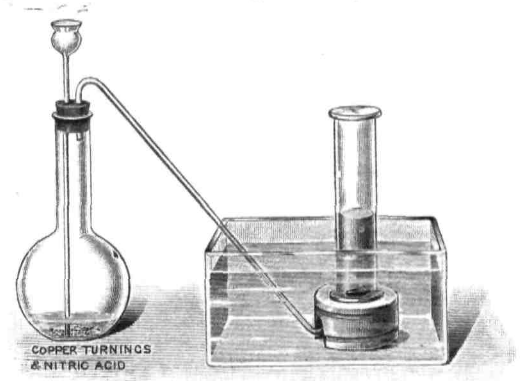


FIG. 157.—PREPARATION OF NITRIC OXIDE.

(*b*) *By Decomposition of Higher Oxides of Nitrogen.*—Nitric oxide is set free as a gas when nitrogen peroxide is decomposed by the action of water,

$$3NO_2 + H_2O = NO + 2HNO_3.$$

It can be prepared very readily by the action of an acid on a nitrite, when nitrous acid is set free and decomposes thus:

$$3HNO_2 = 2NO + HNO_3 + H_2O.$$

(*c*) *By Oxidation of Nitrogen.*—Nitric oxide is produced on a very large scale by the action of an electric discharge on air:

$$N_2 + O_2 \rightleftharpoons 2NO - 2 \times 21{,}600 \text{ calories.}$$

Nitric oxide is a strongly endothermic compound and its preparation from nitrogen and oxygen is in many respects analogous to the preparation of ozone from oxygen; but as nitric oxide is far more stable than ozone, it is not necessary to chill the gas either so rapidly or to so low a temperature after heating it, and a much heavier electric discharge can therefore be employed.

The conditions of equilibrium at different temperatures have been found to be as follows:

TABLE 45.—OXIDATION OF NITROGEN AND DISSOCIATION OF NITRIC OXIDE.

	$N_2 + O_2$	$\rightleftharpoons$ 2NO.
At 1500°	$99\frac{2}{3}$%	$\frac{1}{3}$%
At 1930°	99	1
At 2300°	98	2
At 3000° (about)	95	5

In order to secure a good yield, it is necessary to heat the air to the highest possible temperature and then to fix the nitric oxide by cooling quickly to 1200°, below which temperature the nitric oxide is no longer liable to decompose.

(*a*) In the process of BIRKELAND and EYDE a high-tension arc, *A* (Fig. 158), passing between water-cooled copper tubes, *BB*, 8 mm. apart, is spread into a large disc by the influence of a magnetic field. This drives the arc away from the centre until it has reached a length of several feet, when the arc goes out and a fresh arc is formed between the terminals. When an alternating current is used, as indicated diagrammatically in Fig. 158, the arcs are displaced alternately upwards and downwards and a circular sheet or disc is produced. The separate arcs cannot be distinguished with the eye, but if a piece of paper be inserted it is pierced by the arc in such a way as to suggest the effect of sparks much more than that of the low-tension arcs which are used for electric light.

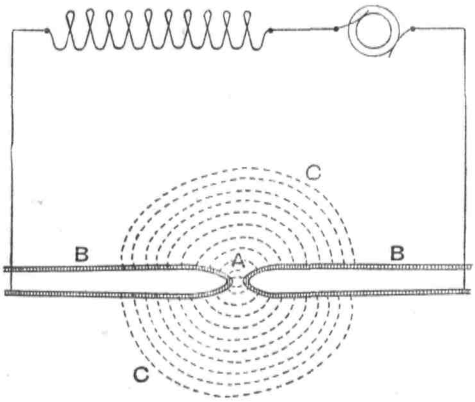


FIG. 158.—DIAGRAMMATIC REPRESENTATION OF BIRKELAND-EYDE PROCESS.

The general structure of the furnace is shown in Fig. 159, where *AA* represent the poles of the electromagnet and *BB* the windings. The air blown in at *C* is admitted laterally, through holes in the fireclay lining, to the sheet of arc radiating from *E*, and escapes from the periphery at *D*. A single furnace may take as much as 3000 kilowatts, or about 4000 horse-power, using an electric current under a pressure of 5500 volts. The product from the furnace consists of air at a temperature of about 1000°, containing about 1·5 per cent. of nitric oxide. The hot gases are used first to heat a series of steam boilers, whereby they are cooled to about 200°. Nitrogen peroxide begins to form as soon as the temperature falls below about 800°, but the oxidation is not quite

complete even at 200°. In the presence of water, however, a complete oxidation to nitric acid can be effected as described above (p. 391).

In the PAULING PROCESS an arc is struck between two "ignition-knives," *C*, mounted on a pair of diverging horns, *A*, arranged after the manner of a lightning arrester (Fig. 160). The arc spreads to the top of the horns and goes out, but is followed by other arcs giving rise to a flame about 75 cm. in height. The upward movement of the arc is assisted by a blast of air, which becomes charged with oxides of nitrogen as in the Birkeland-Eyde process. The form of the horns used for

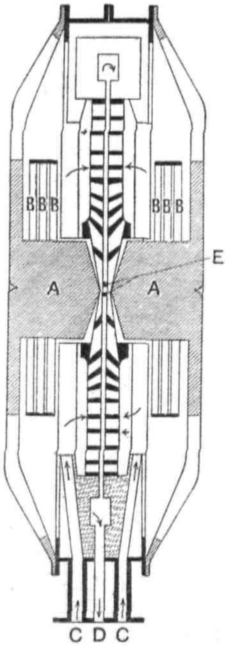


FIG. 159.—BIRKELAND-EYDE FURNACE.

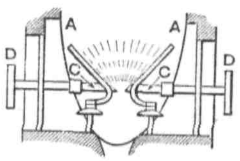


FIG. 160.—PAULING ARC.

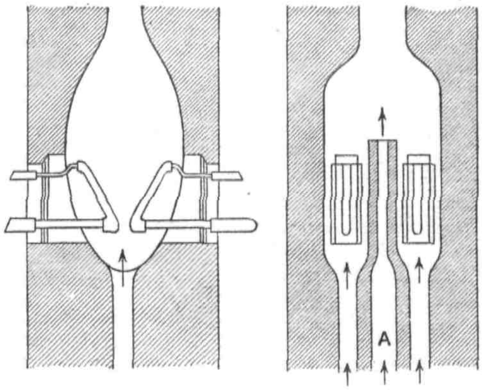


FIG. 161.—PAULING FURNACE. (After Allmand.)

production on a large scale is shown in Fig. 161. Two arcs are arranged in series and the products are cooled by mixing with a jet of air, *A*, which has already passed through the arc.

(*b*) The dilute nitric acid obtained by absorbing the gases in water may be concentrated by distilling it from 92 per cent. sulphuric acid, but most of it is converted into calcium nitrate by the action of chalk, and used in this form either as a fertiliser or for the preparation of ammonium nitrate (p. 606). Nitrites may be obtained instead of nitrates by absorbing the hot gases in soda at 200° to 300° when they have oxidised to an extent corresponding with the formula N_2O_3.

Physical Properties and Solubility of Nitric Oxide.

Nitric oxide is a colourless gas which boils at — 150° and freezes at — 160° (compare methane, b.-pt. — 164°, f.pt. — 186°) ; its properties are therefore intermediate between those of nitrous oxide (b.-pt. — 90°, m.-pt. — 102°) on the one hand, and of nitrogen and oxygen on the other. It is only sparingly soluble in cold water, which dissolves 6 per cent. of its volume at 8°, as compared with 4 per cent. of oxgyen and 2 per cent. of nitrogen or hydrogen.

It is freely soluble in solutions of ferrous salts, giving a dark brown liquid which probably contains an unstable nitroso-compound, *e.g.*, $FeCl_2NO$. The production of this dark brown compound by the action of ferrous sulphate on nitric acid is used in the BROWN RING TEST for nitric acid, *e.g.*, by pouring sulphuric acid cautiously down the side of a test-tube containing a mixture of ferrous sulphate with the liquid to be tested, when a brown colour appears at the boundary between the two layers if nitric acid is present. When the dark liquid is heated the nitric oxide escapes and the brown colour disappears. The solubility of nitric oxide in aqueous solutions of ferrous sulphate has been used since the time of Priestley to estimate the purity of nitric oxide and as a means of preparing pure samples of the gas. At the present time, however, the gas can be purified more effectively and on a large scale by fractional distillation of the liquid.

Chemical Properties of Nitric Oxide.

(*a*) *Reduction.*—Although nitric oxide is an endothermic compound and contains more than 50 per cent. by weight of oxygen, it is not very effective either as an oxidising agent or as a supporter of combustion. Thus, phosphorus in vigorous combustion will continue to burn in the gas, but it extinguishes burning charcoal and sulphur. The gas is, however, reduced slowly to nitrous oxide, N_2O, and nitrogen by moist iron filings or by a mixture of iron filings and sulphur (Priestley, 1775). It is also reduced to nitrogen by prolonged heating with charcoal or iron (Priestley, 1786), or by burning potassium in the gas. By the action of tin and hydrochloric acid it is reduced to hydroxylamine,

$$NO + 3H = NH_3O.$$

(*b*) *Additive Compounds.*—Nitric oxide combines with oxygen to form nitrogen peroxide (p. 411),

$$2NO + O_2 = N_2O_4.$$

It unites with chlorine in presence of charcoal to form nitrosyl chloride (p. 399),

$$2NO + Cl_2 = 2NOCl,$$

and with bromine to form nitrosyl bromide and nitrosyl tribromide (p. 400),

$$2NO + Br_2 = 2NOBr.$$
$$2NO + 3Br_2 = 2NOBr_3.$$

Its combination with hydrogen to form hydroxylamine and its absorption by ferrous salts may also be regarded as additive actions.

(c) *Decomposition.*—In view of the strongly endothermic character of nitric oxide, its heat of formation being $-$ 21,600 calories, it is remarkable that it should be so stable. No decomposition takes place until the temperature rises to about 1000°, when an almost complete decomposition into its elements takes place,

$$2NO = N_2 + O_2 + 2 \times 21{,}600 \text{ cal.}$$

An alternative decomposition, as shown by the equation

$$4NO = N_2 + 2NO_2 \text{ or } N_2 + N_2O_4,$$

would liberate almost as much heat, since the heat of formation of gaseous nitrogen peroxide, $2NO_2 \rightleftharpoons N_2O_4$, is only $-$ 2 × 1700 calories at 22°, and the heat balance is therefore

$$4 \times 21{,}600 - 2 \times 1700 = 83{,}000 \text{ cal.} = 4 \times 20{,}750 \text{ for } 4NO.$$

A decomposition of this kind occurs in the action on cold nitric oxide of fluorine and of "active nitrogen" (p. 363), gaseous nitrogen being liberated in each case, whilst the nitrogen dioxide becomes united with fluorine or with nitric oxide as shown in the equations

$$4NO + F_2 = N_2 + 2NO_2F.$$
$$3NO + N = N_2 + NO_2{\cdot}NO \text{ or } N_2O_3.$$

Reduction and Volumetric Composition of Nitric Oxide.

The oxygen of nitric oxide can be removed quantitatively by the prolonged action of heated charcoal or iron (Priestley, 1786), or more readily by the action of potassium (Gay-Lussac, 1809). Under these conditions a residue of nitrogen is produced equal to one-half the volume of the nitric oxide.

$$\underset{2\ vols.}{2NO} + C = \underset{1\ vol.}{N_2} + \underset{1\ vol.}{CO_2}$$

$$\underset{2\ vols.}{2NO} + 2Fe = \underset{1\ vol.}{N_2} + 2FeO$$

$$\underset{2\ vols.}{2NO} + 4K = \underset{1\ vol.}{N_2} + 2K_2O.$$

As the gas contains half its volume of nitrogen, and its density is almost exactly the average of those of nitrogen and oxygen, nitric oxide is evidently formed without contraction by the combination of equal volumes of nitrogen and oxygen.

$$\underset{1\ vol.}{N_2} + \underset{1\ vol.}{O_2} = \underset{2\ vols.}{2NO}$$

Gravimetric Composition of Nitric Oxide.

A complete gravimetric analysis of nitric oxide was made by Gray in 1905, by reducing the oxide with nickel and weighing

both the oxygen absorbed by the nickel and the nitrogen set free.

The flask *A* (Fig. 162) was provided with a glass stopper, *B*, leading through a stopcock to a capillary ground-glass joint, *D*. A small platinum boat, *H*, containing finely-divided nickel, was surrounded by a coil of platinum wire, which could be heated to any desired temperature by an electric current, supplied through the stout platinum electrodes, *EE*. The bulb *M*, containing charcoal, and provided with a stopcock, could be connected with the bulb *A* through the capillary ground-glass joints at *K* and *D*. Air could be pumped out or nitric oxide admitted through the stopcock, *P*.

The bulb *A* was weighed (i) empty, and (ii) filled with nitric oxide. After burning the nickel in the boat *H*, the nitrogen left in the bulb *A* was transferred to the bulb *M* by opening the two stopcocks (after pumping out the air between *K* and *D*) and then cooling the charcoal in *M* by liquid air. The whole of the nitrogen was thus condensed on the charcoal and a vacuum was produced in the rest of the apparatus. A third weighing of the bulb *A* gave the weight of oxygen which had been taken by the nickel from the nitric oxide, whilst the increase in the weight of the bulb *M* gave the weight of the nitrogen that had been set free, as shown in the equation

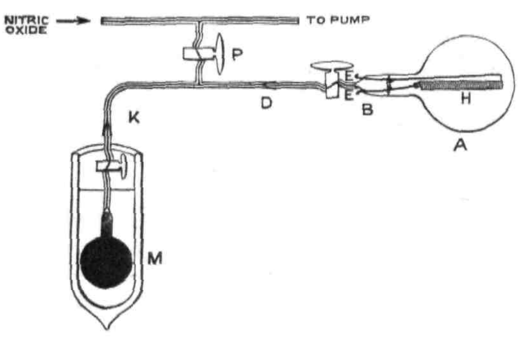


FIG. 162.—GRAY'S APPARATUS FOR DETERMINING THE GRAVIMETRIC COMPOSITION OF NITRIC OXIDE.

$$2NO + 2Ni = N_2 + 2NiO.$$

In a typical experiment,

$$0{\cdot}62103 \text{ gram of nitric oxide gave } \begin{cases} 0{\cdot}33103 \text{ gram of oxygen} \\ 0{\cdot}28998 \text{ gram of nitrogen,} \end{cases}$$

whence 14·013 grams of nitrogen combine with 16 grams of oxygen to form 30·013 grams of nitric oxide.

Combination of Nitric Oxide with Oxygen.

The oxidation of nitric oxide by oxygen was used by Priestley to estimate the " goodness " of air, *i.e.*, the proportion of oxygen which it contains. Equal volumes of nitric oxide and air were mixed in a eudiometer (p. 368), consisting of a narrow, graduated glass tube standing over water, and the contraction of volume was measured. The method is, however, uncertain, on account of the variety of products that may be formed, thus

(i) When the dry gases are mixed nitrogen peroxide is produced,

$$\underset{2\ vols.}{2NO} + \underset{1\ vol.}{O_2} = 2NO_2 \text{ or } N_2O_4.$$

(ii) By slow absorption over water in a narrow tube, nitric acid is formed (compare p. 390),

$$\underset{4\ vols.}{4NO} + \underset{3\ vols.}{3O_2} + 2H_2O = 4HNO_3.$$

(iii) By rapid absorption over potash a nitrite is produced,

$$\underset{4\ vols.}{4NO} + \underset{1\ vol.}{O_2} + 4KOH = 4KNO_2 + 2H_2O$$

The extreme cases, given under (ii) and (iii), show the combination of 133 and 400 parts by volume of nitric oxide with 100 parts of oxygen, and were used by Gay-Lussac in establishing for the first time the correct composition of nitric and nitrous acids. The proportions of nitric oxide and oxygen which combine together over water may, however, have almost any value between these extreme limits. In commercial practice, nitric oxide is commonly oxidised completely to nitric acid as shown under (ii).

Preparation of Nitrous Oxide or Dinitrogen Monoxide, N_2O.

(*a*) Nitrous oxide was first prepared by Priestley in 1775, by the action of moistened iron filings or of iron filings and sulphur on nitric oxide,

$$2NO + Fe + H_2O = N_2O + Fe(OH)_2.$$

He also obtained it from the liquid produced by the action of zinc on

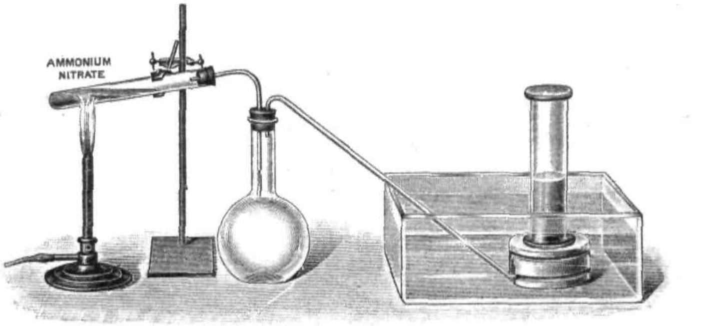


FIG. 163.—PREPARATION OF NITROUS OXIDE.

cold dilute nitric acid ; the gas is soluble in cold water and was separated by heating the liquid gently.

(*b*) Berthollet in 1785 prepared the gas in a purer form by heating ammonium nitrate,

$$NH_4NO_3 = 2H_2O + N_2O.$$

The nitrate (Fig. 163) must be free from organic impurities and ammonium chloride in order to prevent the formation of carbonic anhydride and

chlorine. A mixture of potassium nitrate and ammonium sulphate may be used in place of the ammonium nitrate.

$$2KNO_3 + (NH_4)_2SO_4 = K_2SO_4 + 2N_2O + 4H_2O.$$

The gas is purified by washing it with an aqueous solution of ferrous sulphate to remove nitric oxide, and is transported commercially in small steel cylinders. In the laboratory it is usually collected over warm water, since it dissolves somewhat readily in cold water.

Properties of Nitrous Oxide.

Nitrous oxide is a colourless, odourless gas. It dissolves in an equal volume of cold water at 6° ; but the solution is neutral and the gas is recovered unchanged on warming.

Nitrous oxide, N_2O, has the same molecular weight as carbon dioxide and the same number of atoms in the molecule. With the exception of the freezing-points, which differ by 45°, the physical properties of the two compounds approximate very closely to one another, and in many instances become almost identical if measured at temperatures 3° lower for CO_2 than for N_2O.

TABLE 46.—PHYSICAL PROPERTIES OF NITROUS OXIDE AND CARBON DIOXIDE.

	N_2O.	CO_2.
Freezing-point	−102°	−57° (5 atm.)
Boiling-point	− 90°	—
Sublimation-point	—	−79°
Critical pressure	75	77 atm.
Critical temperature	35·4°	31·9°
Critical density	0·45	0·46
Density of liquid at 10°	0·856	0·858
Refractive index of liquid n_D^{16}	1·193	1·190
Dielectric constant of liquid, 0°	1·598	1·582
Surface tension of liquid = 2·9 dynes/cm. at	12·2°	at 9·0°
Solubility of gas in water at 0°	1·305	1·780 vols.
Solubility of gas in alcohol at 15°	3·25	3·15 vols.
Viscosity of gas at 20°	148×10^{-6}	148×10^{-6}

Although the ratio of oxygen to nitrogen in nitrous oxide is only half as great as in nitric oxide, and its heat of formation is practically the same (— 20,600 calories for N_2O and — 21,000 calories for NO), it is far more active as a supporter of combustion, and sulphur, phosphorus, charcoal, and a candle burn in it almost as well as in oxygen itself (Priestley) ; it can, however, be distinguished from oxygen by the fact that it does not give rise to any colour or diminution of volume when mixed with nitric oxide.

It can be breathed with impunity for a time and will support respiration. Davy, who discovered this property, found that it produced an exhilarating sensation and that in some cases laughter was caused, thus justifying the name LAUGHING GAS which is sometimes applied to it. It has been used since 1800 as an anæsthetic in dentistry, and more

recently in general surgery, mixed with oxygen and in conjunction with a "local anæsthetic."

Composition of Nitrous Oxide.

Davy determined the composition of nitrous oxide by heating charcoal in it, when it gave half its volume of carbonic anhydride, which was absorbed by alkali, leaving one volume of nitrogen; nitrous oxide therefore contains half its volume of oxygen and its own volume of nitrogen.

$2N_2O$	+	C	=	$2N_2$	+	CO_2
2 vols.				*2 vols.*		*1 vol.* (containing 1 *vol.* of oxygen).

This analysis was confirmed by measuring the density of the gas.

Preparation of Nitrogen Dioxide, NO_2.

(*a*) *From Nitric Oxide.*—When nitric oxide is mixed with air at temperatures below 800° it combines with oxygen to form nitrogen dioxide, NO_2. The action is accompanied by liberation of heat, *e.g.*, at 150°, when the product is all present as NO_2, the heat-balance is shown by the equation

$$NO + \tfrac{1}{2}O_2 = NO_2 + 14{,}000 \text{ calories.}$$

The action is reversible at high temperatures, the proportion of the dioxide diminishing as the temperature rises, thus:

TABLE 47.—OXIDATION OF NITRIC OXIDE AND DISSOCIATION OF NITROGEN DIOXIDE.

	$2NO + O_2$	$\rightleftharpoons 2NO_2$
At 223°	5·3%	94·7%
At 390°	35·1	64·9
At 490°	55	45

(*b*) *From Nitrates of Heavy Metals.*—On a small scale, the same gas is produced by the action of heat on lead nitrate (Fig. 164*a*),

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

The mixed gases are passed into a flask surrounded by a freezing mixture, and purified by redistilling from phosphoric anhydride (Fig. 164*b*), when a pale yellow liquid is produced consisting mainly of **dinitrogen tetroxide,** N_2O_4. Nitrogen dioxide, which is obtained on warming this liquid, cannot be collected over water or over mercury, as it acts upon both these liquids.

Properties of Nitrogen Dioxide.

Nitrogen dioxide is a brown gas with a characteristic absorption spectrum, by means of which it can be recognised and estimated.

Apart from dinitrogen trioxide, which is blue, it is the only coloured oxide of nitrogen, and whenever a brown or yellow colour appears as a result of chemical changes involving the use of nitric acid, it may be

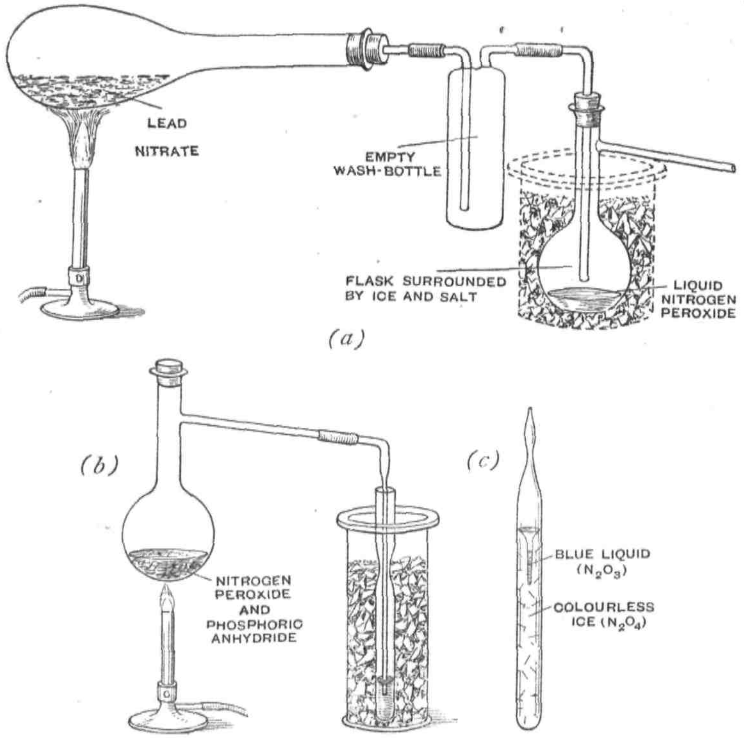


FIG. 164.—PREPARATION OF NITROGEN PEROXIDE.

assumed that nitrogen dioxide has been produced. Thus the brown fumes liberated by the action of nitric acid on metals owe their colour to the presence of nitrogen dioxide,

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O,$$

and the yellow colour which is produced when strong nitric acid is exposed to light is due to the liberation of nitrogen dioxide,

$$4HNO_3 = 2H_2O + 4NO_2 + O_2.$$

Association and Dissociation in Nitrogen Peroxide.

Priestley noticed that the colour of nitrogen dioxide almost disappeared when the gas was cooled, but reappeared again when the gas was heated. Playfair and Wanklyn in 1862 showed that the loss of

colour is due to the conversion, by a balanced action, of the brown nitrogen dioxide into a colourless dinitrogen tetroxide,

$$2NO_2 \underset{\text{HOT}}{\overset{\text{COLD}}{\rightleftharpoons}} N_2O_4.$$

The mixture of gases represented by this equation is conveniently described as **nitrogen peroxide.** Playfair and Wanklyn measured the density of the gas at different temperatures and calculated the proportions by weight of the two oxides to be as follows:

TABLE 48.—DISSOCIATION OF NITROGEN PEROXIDE.

	$2NO_2$ ⇌	N_2O_4.
At 26·7° . . .	20%	80% (approximately)
At 49·6° . . .	40	60
At 100·1° . . .	89	11
At 154·0° . . .	100	0

During the dissociation the specific heat of the gas is increased enormously by the heat of dissociation of the tetroxide. Thus, between 27° and 67°, when the dissociation is proceeding very rapidly, the molecular heat (p. 140), which should be about 8 calories for a triatomic gas expanding at constant pressure, is increased to 75 calories (for 46 grams of NO_2); but this diminishes to 9 calories in the range from 150° to 200° when dissociation is complete.

The gas condenses to a pale yellow liquid boiling at 22°. This can scarcely contain more than perhaps 1 per cent. of the brown dioxide. As the liquid is cooled the colour diminishes still further, and the solid which separates at – 10° (Fig. 164*c*) is an absolutely colourless ice which must be regarded as pure **dinitrogen tetroxide,** N_2O_4, just as the gas above 150° consists wholly of **nitrogen dioxide**, NO_2.

Chemical Properties of Nitrogen Peroxide.

(*a*) *Action of Alkalies and of Water.*—Nitrogen peroxide is not a simple anhydride, but when it is dissolved in alkalies, it gives a mixture of nitrate and nitrite in equivalent quantities,

$$2KOH + N_2O_4 = KNO_3 + KNO_2 + H_2O.$$

A similar action takes place in the presence of water, but as nitrous acid is unstable, the ultimate action is to produce nitric acid and nitric oxide,

$$2H_2O + 3N_2O_4 = 4HNO_3 + 2NO.$$

In the presence of oxygen and water, nitrogen peroxide is converted completely into nitric acid,

$$2H_2O + 2N_2O_4 + O_2 = 4HNO_3.$$

(*b*) *Action on Metals and Metallic Oxides.*—Some metals absorb nitrogen peroxide, giving rise to nitric oxide and a nitrate; thus potassium catches fire in the gas

$$K + N_2O_4 = KNO_3 + NO,$$

sodium and mercury are attacked rapidly, but without the production of flame, and lead is attacked slowly. Metallic oxides absorb nitrogen peroxide and are converted into a mixture of nitrite and nitrate, *e.g.*, at 200° baryta becomes incandescent, owing to the action shown in the equation

$$2BaO + 2N_2O_4 = Ba(NO_2)_2 + Ba(NO_3)_2.$$

(*c*) *Nitrogen Peroxide as an Oxidising Agent and as a Carrier of Oxygen.*—Although it contains twice as much oxygen as nitric oxide, nitrogen peroxide is very reluctant to part with it and does not readily support combustion. Phosphorus, charcoal, and potassium will burn in the gas, which is thus reduced to gaseous nitrogen. In other cases, however, nitric oxide is the chief product of reduction; in contact with air this is at once re-oxidised to the dioxide, and the process of reduction and oxidation may then proceed indefinitely. When used thus as a means of transferring oxygen from the air to a reducing agent, nitrogen peroxide is described as a CARRIER OF OXYGEN. It is used in this way in the lead-chamber process for the manufacture of sulphuric acid (p. 343). Again, when ozone or a cupric salt is estimated by its power of liberating iodine from potassium iodide, the presence of oxides of nitrogen is fatal to the analysis because they are capable of re-oxidising the iodide, and under some conditions (*e.g.*, in acid solutions) of "carrying" atmospheric oxygen to the iodide and so causing the oxidation to proceed indefinitely.

$$NO_2 + 2HI = NO + I_2 + H_2O.$$
$$2NO + O_2 = 2NO_2$$

Composition of Nitrogen Peroxide.

Gay-Lussac in 1816 determined the composition of nitrogen peroxide by mixing measured volumes of nitric oxide and oxygen. As this cannot be carried out either over water or over mercury, Gay-Lussac measured the contraction produced by admitting (i) oxygen to an exhausted bulb into which he had introduced a known quantity of nitric oxide and (ii) nitric oxide to a bulb containing a known quantity of oxygen. He found a contraction of 94 volumes when 100 volumes of nitric oxide were mixed with an excess of oxygen and a contraction of 192 volumes when 100 volumes of oxygen were mixed with an excess of nitric oxide. These figures agree approximately with the values required by the equation

$$\underset{2\ vols.}{2NO} + \underset{1\ vol.}{O_2} = \underset{1\ vol.\ (contraction\ 2\ vols.),}{N_2O_4}$$

namely, a contraction *equal to the volume of nitric oxide used* or *one-half the volume of oxygen used*; but the contraction in each case was rather less than this, because some of the nitrogen peroxide remained in the form of nitrogen dioxide, NO_2.

Nitrous Anhydride or Dinitrogen Trioxide, N_2O_3.

(*a*) *Preparation.*—Nitrous anhydride is best prepared by the interaction of nitric oxide and nitrogen peroxide,

$$NO + NO_2 = N_2O_3.$$

Thus, it can be produced by passing oxygen gas through liquid nitric oxide,

$$4NO + O_2 = 2N_2O_3,$$

or by passing gaseous nitric oxide into liquid nitrogen peroxide,

$$2NO + N_2O_4 = 2N_2O_3.$$

A suitable mixture of nitric oxide and nitrogen peroxide can also be prepared by the action of arsenious oxide on nitric acid,

$$2HNO_3 + 2H_2O + \underset{\text{Arsenious oxide}}{As_2O_3} = \underset{\text{Arsenic acid}}{2H_3AsO_4} + NO + NO_2.$$

(*b*) *Properties.*—Nitrous anhydride condenses to blue crystals melting at $-103°$, but, like dinitrogen tetroxide, N_2O_4, it begins to dissociate as soon as it melts,

$$2N_2O_3 \rightleftharpoons 2NO + N_2O_4,$$

giving rise to two colourless oxides of nitrogen. The blue colour of the nitrous anhydride persists almost up to 0°, but when the temperature rises further, brown nitrogen dioxide begins to be formed by the dissociation of the colourless tetroxide, N_2O_4, and the blue colour of the liquid (Fig. 164 (*c*), p. 412) changes to green.

The liquid mixture of nitrous anhydride with the products of its dissociation, as shown in the preceding equation, usually boils at $-2°$, but by carefully drying it Baker succeeded in raising the boiling-point to $+43°$ and obtained a liquid which remained blue to a higher temperature than before. The vapour from the dry liquid was red, but condensed to a blue liquid; its density was much greater than that required by the formula N_2O_3, the values being a little higher than those required by the formula N_4O_6 (compare P_4O_6). Even when not specially dried, nitrous anhydride probably persists to a small extent in the gaseous state, since the expansion which results from diluting nitrogen peroxide with nitric oxide is less than that produced by dilution with inert gases such as nitrogen and carbon dioxide.

Nitric Anhydride or Dinitrogen Pentoxide, N_2O_5.

(*a*) *Preparation.*

(i) Nitric anhydride was first prepared by Deville by the action of dry chlorine on solid silver nitrate at 60°,

$$4AgNO_3 + 2Cl_2 = 4AgCl + O_2 + 2N_2O_5.$$

(ii) It is prepared most readily by the action of phosphoric anhydride on nitric acid of density 1·5, as represented by the symmetrical equation

$$2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3.$$

The phosphoric oxide is added gradually to well-cooled nitric acid; the syrupy mixture is distilled, and the orange-coloured distillate

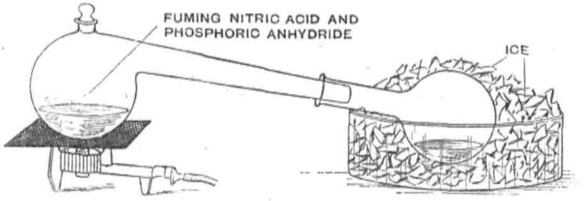


FIG. 165.—PREPARATION OF NITRIC ANHYDRIDE.

cooled by a freezing mixture (Fig. 165), when crystals slowly separate. These are drained and the mother liquor is pressed out; they are then remelted and recrystallised.

(iii) Nitric anhydride is formed as a product of the action of ozone on nitrogen peroxide,

$$N_2O_4 + O_3 = N_2O_5 + O_2.$$

During this action two new absorption bands appear on the absorption spectrum of the nitrogen peroxide, and these have been attributed to a higher oxide, to which the name **pernitric anhydride** has been assigned, to correspond with the persulphuric anhydride obtained in a similar manner from sulphuric anhydride (p.347).

(b) Properties.—Nitric anhydride forms colourless, glistening prisms which melt with slight decomposition at 30° to a yellow liquid. It decomposes still further when it boils at about 50°. Decomposition is accelerated by

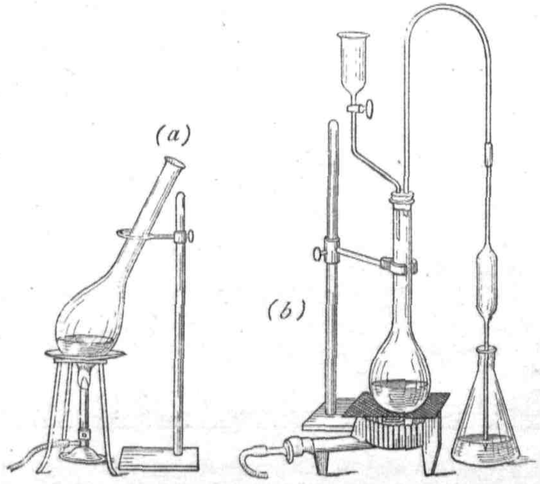


FIG. 166.—KJELDAHL'S APPARATUS FOR ESTIMATION OF NITROGEN.

light. The anhydride combines with water to form nitric acid and with aqueous ammonia to form ammonium nitrate.

$$N_2O_5 + H_2O = 2HNO_3.$$
$$N_2O_5 + 2NH_4OH = 2NH_4NO_3 + H_2O.$$

It is a powerful oxidising agent and attacks organic substances with great violence, so that it can only be handled in apparatus composed entirely of glass without corks or rubber connections.

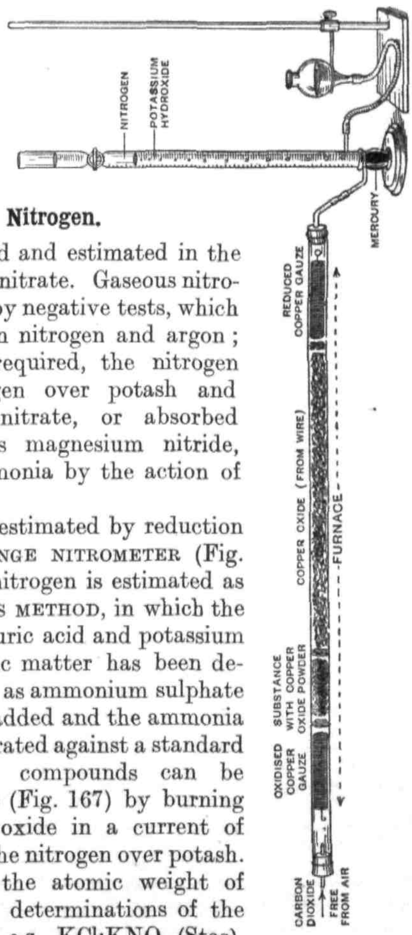


FIG. 167.—DUMAS' APPARATUS FOR ESTIMATION OF NITROGEN.

Detection and Estimation of Nitrogen.

Nitrogen is usually detected and estimated in the form either of ammonia or of a nitrate. Gaseous nitrogen is identified as a rule only by negative tests, which would not distinguish between nitrogen and argon; when positive evidence is required, the nitrogen may be sparked with oxygen over potash and converted into potassium nitrate, or absorbed by means of magnesium as magnesium nitride, Mg_3N_2, and liberated as ammonia by the action of water.

Oxidised nitrogen is usually estimated by reduction to nitric oxide, *e.g.*, in a LUNGE NITROMETER (Fig. 155, p. 396), whilst reduced nitrogen is estimated as ammonia, *e.g.*, by KJELDAHL'S METHOD, in which the material is heated with sulphuric acid and potassium sulphate until all the organic matter has been destroyed and the nitrogen fixed as ammonium sulphate (Fig. 166*a*); an alkali is then added and the ammonia distilled out (Fig. 166*b*) and titrated against a standard acid. Nitrogen in organic compounds can be estimated by DUMAS' METHOD (Fig. 167) by burning the compound with copper oxide in a current of carbon dioxide and collecting the nitrogen over potash.

The accepted value for the atomic weight of nitrogen is based mainly on determinations of the *ratios of nitrates to chlorides, e.g.*, $KCl:KNO_3$ (Stas), on the ratio $NH_4Br:Ag$ (Scott), on the analysis of nitric oxide (Gray, p. 408), and on exact determinations of the density and molecular weight of nitrous and nitric oxides (Guye, p. 142).

CHAPTER XXVII

15. PHOSPHORUS. P=31·04

Occurrence.

(*a*) *Mineral Phosphates.*—Phosphorus is found to the extent of about 0·13 per cent. (or 0·3 per cent. P_2O_5) in igneous rocks as APATITE (Fig. 228, p. 624) or **calcium fluorphosphate**, $3Ca_3(PO_4)_2,CaF_2$, or $Ca_5(PO_4)_3F$. This is a very stable mineral and (after zircon) is one of the first to crystallise from the molten magma; it also appears as a crystalline constituent of basic slags (p. 769) containing phosphorus, when fluorspar, CaF_2, has been used as a flux. The fluorine in this compound may be replaced vicariously by an equivalent amount of chlorine, giving ultimately a CHLORO-APATITE, $Ca_5(PO_4)_3Cl$, or in part by hydroxyl, OH; isomorphous compounds are also found in which the calcium is replaced by lead and the phosphorus by arsenic or by vanadium, as in VANADINITE, $Pb_5(VO_4)_3Cl$, in which every element of the apatite except oxygen has been replaced by an isomorphous element.* **Ferric phosphate**, $FePO_4$, and **aluminium phosphate**, $AlPO_4$, are found in various forms, mainly as earthy deposits, but also including crystalline minerals such as TURQUOISE, $AlPO_4,Al(OH)_3,H_2O$. The "rare earths" (Chapter XXXIV) are also found as phosphates; thus, MONAZITE contains an isomorphous mixture of phosphates such as $CePO_4$, $LaPO_4$, etc., with silicates such as $ThSiO_4$ which are isomorphous with these phosphates. The phosphorus in iron ores passes with the metal into the pig iron, but is removed in combination with lime as BASIC SLAG when the iron is converted into steel; this form of phosphorus has been found to have a very remarkable effect in improving poor pasture land, mainly by promoting the growth of clover, which is able to assimilate atmospheric nitrogen and is therefore independent of nitrogenous manures.

(*b*) *Organic Compounds.*—Phosphorus is an important minor constituent of plants and is essential to their growth. It is also a normal constituent of animal tissues and is particularly abundant in bones, which when calcined yield a BONE-ASH consisting almost entirely of **calcium phosphate**, $Ca_3(PO_4)_2$; but since mineral phosphates cannot be assimilated by animals, they are dependent for their supplies of

* Compare Wöhler's celebrated skit on substitution (1840) in which he describes the conversion of manganese acetate, $MnO,C_4H_6O_3$, into $Cl_2Cl_2,Cl_8Cl_6Cl_6$. (*Historical Introduction to Chemistry*, p. 414.)

phosphorus on the synthetic work of plants, just as they are for their supplies of available nitrogen. The phosphorus absorbed by the plant is largely concentrated in the seed and is therefore removed from the soil with the crops. When the crops are eaten in the fields, or on the farm, by cattle, sheep, or horses, much of the phosphorus is excreted and returned to the soil as liquid or solid farmyard manure; but phosphorus is also present in dairy produce, such as milk and cheese, as well as in meat and in bones, and is therefore constantly being sent away even when the crops are mainly consumed on the farm. This removal of phosphorus resulted in a most serious loss of fertility in the English pasture lands during the early part of the nineteenth century; their fertility was, however, restored by manuring with bones, which were collected for this purpose from the battlefields of Europe. More recently it has been discovered that the production of natural indigo depends more on the supply of phosphates than on any other single factor.

(c) *Phosphatic Rocks.*—In addition to farmyard manure, the excrements of birds collected from islands in the Pacific Ocean under the name of GUANO are an important source of phosphorus for agriculture. Still larger supplies are, however, derived from phosphate rocks, many of which are believed to have been formed by the decay of animal excrements in presence of lime, giving rise to ill-defined earthy minerals, containing calcium phosphate, $Ca_3(PO_4)_2$, to which the name of PHOSPHATITE is given. Phosphorus may also be fixed in the form of aluminium phosphate, $AlPO_4$, and ferric phosphate, $FePO_4$, as described above, when soluble phosphates are brought into contact with rocks rich in these elements but not containing much chalk.

Preparation of Phosphorus.

Phosphorus was first prepared about 1674 by Brand by distilling evaporated urine with sand. Scheele in 1775 prepared it by distilling phosphoric acid with charcoal, and this method of preparation was subsequently developed on a large scale.

The phosphoric acid was liberated from calcium phosphate, $Ca_3(PO_4)_2$, by adding the right amount of sulphuric acid to decompose the phosphate and any carbonate that might be present,

$$\underset{\text{Calcium phosphate}}{Ca_3(PO_4)_2} + \underset{\text{Sulphuric acid}}{3H_2SO_4} = \underset{\text{Calcium sulphate}}{3CaSO_4} + \underset{\text{Phosphoric acid}}{2H_3PO_4}.$$

The acid was drained off on filter-beds from the insoluble residue of calcium sulphate, which was dried for use in manures; the solution was concentrated to a syrup, mixed with coke or charcoal, and ignited until the phosphoric acid was converted into metaphosphoric acid, HPO_3 (compare nitric acid, HNO_3),

$$H_3PO_4 = HPO_3 + H_2O.$$

The reduction of the metaphosphoric acid by distillation is represented by the equation

$$4HPO_3 + 12C = P_4 + 2H_2 + 12CO.$$

This action is analogous to the preparation of sodium from its hydroxide (p. 556),

$$2NaOH + 2C = 2Na + H_2 + 2CO,$$

and of zinc from its oxide (p. 868) by distillation with carbon, and was carried out in a somewhat similar plant, Fig. 168. Fireclay retorts about 3 feet in length and 8 inches in diameter were used, the mouth being tapered to about 3 inches; a 2-inch iron pipe was luted into the mouth of the retort and led the vapour down into a trough, where it was condensed under water.

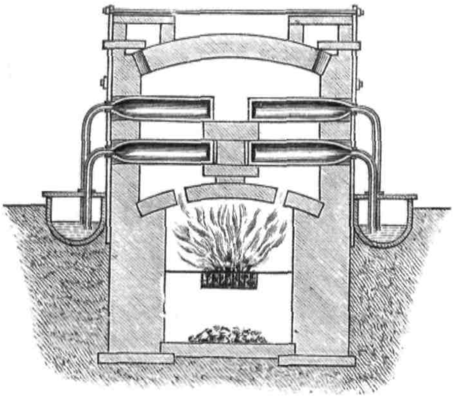


FIG. 168.—FURNACE FOR MANUFACTURE OF PHOSPHORUS.

By making use of an electric furnace the preliminary separation of the phosphoric acid by sulphuric acid is now avoided, the base being removed in combination with silica as a slag,

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C = 6CaSiO_3 + P_4 + 10CO.$$

The crude phosphorus is melted under hot water in order to separate it from clay and sand, purified by oxidation with chromic acid, filtered through a canvas bag to remove mechanical impurities, cast into wedges or sticks, and packed with water in soldered tins.

Properties of Phosphorus.

(*a*) *Physical Properties.*—Phosphorus, in its ordinary form, is a translucent solid, often of a pale yellow colour, which is soft when warm, but brittle when cold. It melts at 44° and boils at 287°. The density of the vapour at temperatures up to 1000° corresponds with the formula P_4, but above 1500° the vapour-density diminishes, and molecules of P_2 are perhaps formed.

White phosphorus is insoluble in water, but freely soluble in carbon disulphide, which dissolves more than four times its weight of phosphorus at 0° and nearly nine times its weight of phosphorus at 10°; the solution deposits brilliant rhombic crystals, which can also be obtained by sublimation of phosphorus in a vessel from which oxygen is excluded. Ether dissolves about 1 per cent. of phosphorus.

(*b*) *General Properties.*—White phosphorus is extremely poisonous, doses of about 0·1 gram producing a fatal effect. Constant exposure to the vapour also leads to chronic poisoning, giving rise to necrosis, especially of the jaw; for this reason the industrial use of white phosphorus for making matches has been prohibited.

Phosphorus derives its name (Greek φῶς, light, φέρω, I carry) from the fact that it glows in the dark, as the result of a slow combustion which gives rise to phosphorous acid, H_3PO_3, and then phosphoric acid, H_3PO_4, together with ozone and hydrogen peroxide. When exposed to air it is liable to melt and take fire spontaneously, and is therefore stored under water; it also takes fire spontaneously when a solution in carbon disulphide is allowed to evaporate on a filter-paper. It is a curious fact that phosphorus is not luminous and is not oxidised in pure oxygen at atmospheric temperatures; but it begins to glow when the pressure is reduced, or when the oxygen is diluted with other gases.

Allotropy of Phosphorus.

Although WHITE PHOSPHORUS is always obtained when phosphorus is distilled, it is not the most stable form of the element. Thus, when exposed to light or to an electrical discharge, or when heated either alone or with a small quantity of iodine, it is converted into RED PHOSPHORUS (von Schrötter, 1845). More drastic treatment, *e.g.*, by heating with lead in a sealed tube, and then removing the metal with acid, converts it into VIOLET OR METALLIC PHOSPHORUS (Hittorf, 1865).

(*a*) *Red phosphorus* is prepared by heating yellow phosphorus to about 240° for several hours in a vessel provided with a narrow tube running through the cover to act as a safety valve. It is ground under water, and freed from yellow phosphorus by extracting with caustic soda. It has no taste or smell and is not poisonous; it is therefore used instead of white phosphorus in making matches, and for other industrial purposes. It is denser than white phosphorus, and differs from it in being insoluble in carbon disulphide. It is much less active in its chemical behaviour, as might perhaps be expected, since the formation of 31 grams of red phosphorus from white phosphorus is accompanied by the liberation of 3700 calories.

(*b*) *Violet phosphorus.*—Red phosphorus is apparently only an intermediate stage in the conversion of white phosphorus into violet or metallic phosphorus. Thus, the densities of the three forms are as follows:

White phosphorus .	1·83
Red „ .	2·15 to 2·34
Violet „ .	2·33

It has therefore been suggested that red phosphorus is simply a solid solution of yellow phosphorus in violet or metallic phosphorus, a

curious case of solid solution which may be compared perhaps with the absorption of antimony chloride by metallic antimony.

When red or violet phosphorus is heated under pressure to 610° it melts to white phosphorus; white phosphorus is also formed from the insoluble modifications by distillation. It is therefore possible that these are polymers of white phosphorus, *e.g.*,

$$\underset{\text{White phosphorus}}{2P_4} \rightleftharpoons \underset{\text{Violet phosphorus}}{P_8},$$

which are decomposed by distillation; but no conclusive evidence is available on this point.

Chemical Properties of Phosphorus.

In its chemical properties, phosphorus shows a strong general similarity to sulphur, whilst its valency brings it into line with nitrogen and arsenic, with which elements it is commonly classified.

(*a*) *Resemblance to Sulphur.*—Sulphur and phosphorus stand almost alone as inflammable non-metals which will burn in oxygen and in chlorine, whereas carbon, which is inflammable in oxygen, will not combine directly with chlorine. Thus,

(i) Phosphorus and sulphur both give two oxides when burnt, and form two principal oxy-acids and two principal series of salts, thus:

Phosphorous oxide, P_4O_6	Sulphur dioxide, SO_2
Phosphorous acid, H_3PO_3	Sulphurous acid, H_2SO_3
Sodium phosphite, Na_3PO_3	Sodium sulphite, Na_2SO_3
Phosphoric oxide, P_4O_{10}	Sulphur trioxide, SO_3
Phosphoric acid, H_3PO_4	Sulphuric acid, H_2SO_4
Sodium phosphate, Na_3PO_4	Sodium sulphate, Na_2SO_4.

(ii) Phosphorus also resembles sulphur in combining directly with halogens, two compounds being formed in each case, *e.g.*,

Phosphorus pentachloride, PCl_5	Sulphur tetrachloride, SCl_4
Phosphorus trichloride, PCl_3	Sulphur monochloride, S_2Cl_2.

(iii) Phosphorus, like sulphur, also unites directly with metals, forming PHOSPHIDES, which are analogous with the oxides and sulphides, *e.g.*, **copper phosphide**, Cu_3P, is used as an alloy with copper in making phosphor-bronze (p. 835). The phosphides are, however, less stable than the sulphides, and some of them resemble the nitrides in being decomposed by water; thus, **calcium phosphide**, Ca_3P_2, which is prepared by the action of phosphorus vapour on red-hot lime, liberates phosphine, PH_3, when acted on by water, as shown in the equation

$$Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3.$$

(iv) Phosphorus and sulphur both dissolve in caustic alkalies, decomposing water and forming a hydride and an oxide or derivatives of these compounds.

(*b*) *Comparison with Nitrogen and Arsenic.*—Whilst phosphorus resembles sulphur more closely than any other element in its general properties, its valency (3 or 5) and the formulæ of many of its compounds correspond with those of nitrogen on the one hand and of arsenic on the other, although these two elements are entirely unlike phosphorus in most of their physical and chemical properties.

(i) The analogy of the formulæ is shown in the following table, *e.g.*,

	Nitrogen.	Phosphorus.	Arsenic.
Elements . . .	N_2	P_4	As_4
Hydrides . .	NH_3	PH_3	AsH_3
	N_2H_4	P_2H_4	—
Chlorides, etc. .	NCl_3	PCl_3	$AsCl_3$
	—	PCl_5	AsF_5
Oxides . . .	N_4O_6	P_4O_6	As_4O_6
	N_2O_5	P_4O_{10}	As_4O_{10}
Acids . . .	HNO_3	HPO_3	—
	—	H_3PO_3	H_3AsO_3
	—	H_3PO_4	H_3AsO_4

(ii) The agreement in valency of these elements leads not merely to analogous formulæ, but also to isomorphism in certain compounds; thus it was in the phosphates and arsenates of sodium, potassium, and ammonium that isomorphism was first discovered, as follows:

Phosphates . .	NaH_2PO_4,H_2O	KH_2PO_4	$(NH_4)H_2PO_4$
Arsenates . .	NaH_2AsO_4,H_2O	KH_2AsO_4	$(NH_4)H_2AsO_4$

(iii) Phosphorus resembles nitrogen in that its hydride, PH_3, instead of being a weak acid like hydrogen sulphide, shows, although in a much smaller degree, the basic properties of ammonia, and forms salts such as phosphonium iodide, PH_4I. The analogy between the hydrides of phosphorus and nitrogen is shown in the following table:—

Phosphine	PH_3	Ammonia	NH_3
Phosphonium iodide	PH_4I	Ammonium iodide	NH_4I
Liquid hydrogen phosphide	P_2H_4	Hydrazine	N_2H_4
Solid hydrogen phosphide	$(P_2H)_n$	Hydrazoic acid	N_3H

Matches.

After many unsuccessful attempts, in which phosphorus played a conspicuous part, to replace the primitive process of igniting tinder by a spark from steel upon flint, the first successful "friction lights" were manufactured in 1827 by John Walker of Stockton-on-Tees; these were splinters of wood dipped in a mixture of potassium chlorate, $KClO_3$, antimony sulphide, Sb_2S_3, and gum, and were ignited by friction between two layers of glass-paper. In order to secure easier ignition, phosphorus was introduced shortly afterwards in place of antimony

sulphide. In order to avoid phosphorus-poisoning, the white phosphorus has been replaced in recent years by red phosphorus (usually the bright red or scarlet form prepared by boiling a solution of ordinary phosphorus in phosphorus tribromide), but at the present time tetraphosphorus trisulphide, P_4S_3, is used almost exclusively. The head of the match therefore usually contains sulphide of phosphorus, with potassium chlorate and manganese dioxide as oxidising agents, glue to act as a "binder," powdered glass or some similar inert material to increase friction, and Prussian blue, chrome yellow, etc., as a colouring matter. In safety matches the head of the match contains the oxidising substances (usually potassium chlorate, potassium dichromate, and red lead) together with antimony sulphide, and sometimes sulphur and charcoal, whilst the composition on the box usually includes red phosphorus.

PHOSPHORUS AND HYDROGEN.

Phosphine, PH_3.

(*a*) *Preparation.*

(i) Phosphine was discovered by Gengembre in 1783, when attempting to prepare a "liver of phosphorus" by the action of alkalies:

$$\underset{}{P_4} + 3KOH + 3H_2O = \underset{\text{Phosphine}}{PH_3} + \underset{\text{Potassium dihydrogen hypophosphite}}{3KH_2PO_2}.$$

This action, which can be carried out by heating phosphorus with

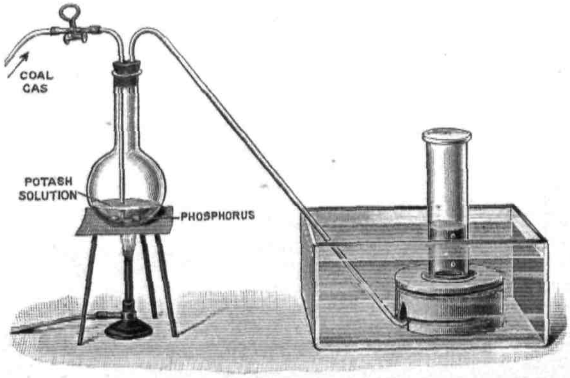


FIG. 169.—PREPARATION OF PHOSPHINE.

caustic potash in a stream of coal gas (Fig. 169), is analogous with the preparation of liver of sulphur,

$$3S + 6KOH = 2K_2S + K_2SO_3 + 3H_2O;$$

but since phosphoretted hydrogen, unlike sulphuretted hydrogen, is not an acid, the hydride escapes as a gas, instead of being held as a phosphide, whilst the oxidised phosphorus is retained as a hypophosphite.

(ii) Phosphine may also be prepared by heating a solution of phosphorous acid. This action involves a simultaneous oxidation and reduction, analogous with that which takes place when potassium chlorate is melted

$$4H_3PO_3 = PH_3 + 3H_3PO_4;$$

$$\text{compare} \quad 4KClO_3 = KCl + 3KClO_4.$$

(*b*) *Properties.*—Phosphine is a gas which condenses to a liquid boiling at $-86°$, when its density is 0·744, and freezing at $-133°$. It is extremely inflammable, burning to water and phosphoric oxide, but when pure it does not inflame spontaneously.

Although its formula is analogous to that of ammonia, phosphine is insoluble in water and does not impart to it an alkaline reaction. It is also devoid of acid properties, and is not absorbed by aqueous potash, soda, or ammonia. It combines, however, with the halogen acids to form salt-like compounds, such as **phosphonium chloride**, PH_4Cl, melting-point 26°, **phosphonium bromide**, PH_4Br, and **phosphonium iodide**, PH_4I. The last compound can be prepared directly by the action of water on iodine and phosphorus, as shown in the empirical equation

$$5I + 9P + 16H_2O = 5PH_4I + 4H_3PO_4.$$

In order to carry out this action, phosphorus and iodine are mixed in a retort in presence of carbon disulphide, which is subsequently removed by distillation; the product is then decomposed with water and the phosphonium iodide sublimed from the retort and condensed in a wide tube. The iodine is here reduced to hydrogen iodide, whilst part of the phosphorus is reduced to phosphine and another part is oxidised to phosphoric acid, in marked contrast to the action of potash, which, in the preparation of phosphine, oxidises the remainder of the phosphorus only to hypophosphite.

Phosphine is a feebly exothermic compound, its heat of formation from white phosphorus being only about 5000 calories; its heat of formation from red phosphorus would therefore be almost zero. It is not formed by the direct combination of phosphorus with hydrogen, and is decomposed by sparking (Dalton)

$$\underset{4\ vols.}{4PH_3} = P_4 + \underset{6\ vols.}{6H_2}$$

Liquid and Solid Hydrogen Phosphide.

(*a*) **Liquid Hydrogen Phosphide**, PH_2 or P_2H_4.—When phosphine is prepared by the action of a hot alkali on phosphorus, or by the action

of water on calcium phosphide, the product is spontaneously inflammable, whereas when prepared from phosphorous acid it does not ignite on exposure to air. The inflammation is due to the presence of a liquid hydride, which can be prepared in quantity by the action of warm water on calcium phosphide made by exposing red-hot lime to the vapour of phosphorus. The hydride condenses readily to a liquid of density 1·01, boiling at 57–58° under 735 mm. pressure. It has the empirical composition PH_2, but is probably P_2H_4, the analogue of hydrazine, N_2H_4, although its vapour density has not been determined.

(*b*) **Solid Hydrogen Phosphide**, P_2H, is formed when liquid hydrogen phosphide is decomposed by exposure to light, by contact with hydrochloric acid, or by heating it above its boiling-point, as shown in the empirical equation

$$\underset{\text{Liquid}}{5PH_2} = \underset{\text{Gas}}{3PH_3} + \underset{\text{Solid}}{P_2H.}$$

The solid product, $(P_2H)_n$, is a yellow powder with feeble acid properties, since it combines with ammonia to form a black compound; it may therefore be regarded as in some respects the analogue of hydrazoic acid, N_3H.

PHOSPHORUS AND OXYGEN.

Oxides and Oxy-acids.

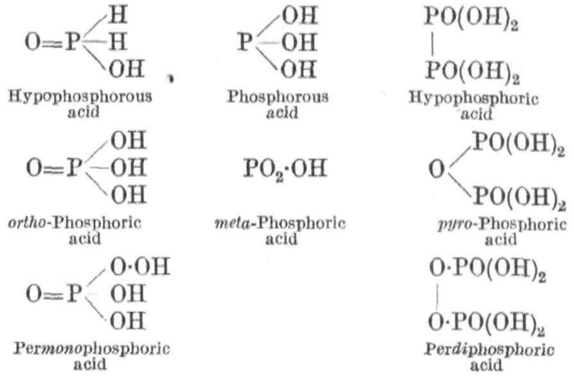
(*a*) Phosphorus forms the following series of oxides and oxy-acids :—

	Hypophosphorous acid, H_3PO_2 $(P_2O + 3H_2O)$
Phosphorous oxide, P_4O_6	Phosphorous acid, H_3PO_3 $(P_2O_3 + 3H_2O)$
Phosphorus dioxide, $(PO_2)_n$	Hypophosphoric acid, $H_4P_2O_6$ $(P_2O_4 + 2H_2O)$
Phosphoric oxide, P_4O_{10}	*ortho*-Phosphoric acid, H_3PO_4 $(P_2O_5 + 3H_2O)$ *meta*-Phosphoric acid, HPO_3 $(P_2O_5 + H_2O)$ *pyro*-Phosphoric acid, $H_4P_2O_7$ $(P_2O_5 + 2H_2O)$
	Per*di*phosphoric acid, $H_4P_2O_8$ $(P_2O_6 + 2H_2O)$
	Per*mono*phosphoric acid, H_3PO_5 $(P_2O_7 + 3H_2O)$

(*b*) The three oxides shown in this table may all be regarded as anhydrides, although the dioxide, like nitrogen peroxide, $N_2O_4 \rightleftarrows 2NO_2$, yields a mixture of acids when acted on by water.

(*c*) Phosphorous and phosphoric acids are tribasic, forming PHOSPHITES, such as Na_3PO_3, and PHOSPHATES, such as Na_3PO_4. Hypophosphorous acid is monobasic, forming only HYPOPHOSPHITES of the type $Na(H_2PO_2)$, like *meta*phosphoric acid, HPO_3, which forms METAPHOSPHATES of the type $(NaPO_3)_n$. *pyro*-Phosphoric acid and per*di*phosphoric acid are tetrabasic and form PYROPHOSPHATES of the type $Na_4P_2O_7$, and PERPHOSPHATES of the type $Na_4P_2O_8$.

(*d*) The structural formulæ of these acids are perhaps as follows :—



Oxides of Phosphorus.

When phosphorus burns in air or oxygen the principal product is phosphoric oxide, P_4O_{10} (see below). When, however, the supply of air is limited a series of lower oxides is produced.

(*a*) A **suboxide** with the formula P_4O has been described as a yellow to red substance resembling red phosphorus in appearance and properties; thus, a product of this kind is formed when phosphorus is burnt in a slow current of air as in (*b*), or when phosphorous oxide is decomposed into the dioxide and a red residue as in (*c*). The existence of this compound is uncertain, and it is possible that the red product is merely an initial stage in the progressive conversion of white or yellow, through red, into violet phosphorus.

(*b*) **Phosphorous oxide** or **phosphorous anhydride**, P_4O_6, can be prepared in substantial quantities by burning phosphorus in the apparatus shown in Fig. 170. The products are filtered through glass-wool and the more volatile portions condensed in a metal tube (*c*) surrounded with water at a temperature of 50–60°. When most of the phosphorus has been burnt, the contents of the tube are melted with steam and strained through another filter of glass-wool before passing into a U-tube (cooled in a freezing mixture) in which the product solidifies again as a waxy mass.

Phosphorous oxide sublimes in feathery crystals, which melt to a mobile liquid, of density 1·936 at 25°. The liquid freezes at + 21°, and boils at 173° in an atmosphere of nitrogen or carbon dioxide. The density of the vapour at 132°, 159°, and 184° (determined by Hofmann's method, p. 38) agrees with the formula P_4O_6; the same formula was also deduced from the freezing-point of a solution of the oxide in benzene.

Phosphorous oxide has a peculiar garlic-like odour resembling that emitted by phosphorus; it is, indeed, quite possible that the odour of

phosphorus and the necrosis produced by the vapour are actually due to this very volatile oxide.* The oxide dissolves slowly in cold water,

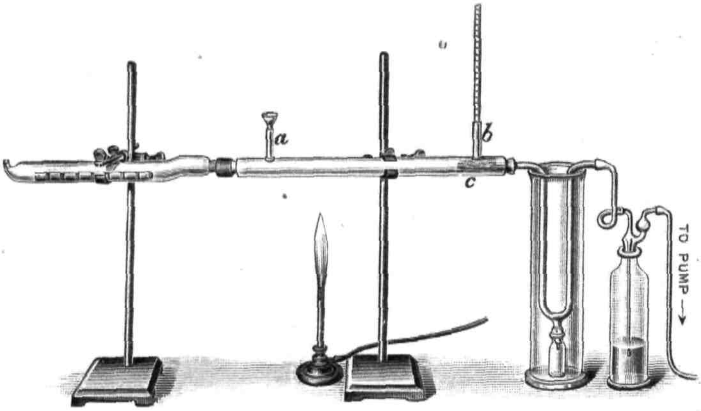


FIG. 170.—APPARATUS FOR PREPARING PHOSPHOROUS OXIDE.

and is then converted gradually into phosphorous acid, H_3PO_3, of which it is the anhydride,

$$P_4O_6 + 6H_2O = 4H_3PO_3.$$

With water at 100° there is an almost explosive liberation of spontaneously inflammable phosphoretted hydrogen, phosphoric acid being also formed, perhaps as shown in the equation

$$P_4O_6 + 6H_2O = PH_3 + 3H_3PO_4.$$

The oxide decomposes when heated above 300° and (unless completely pure) also becomes red, and decomposes in a similar manner, when exposed to light. It oxidises in air or oxygen to phosphoric oxide,

$$P_4O_6 + 2O_2 = P_4O_{10}.$$

The action in dry oxygen is accompanied by a luminous glow, but inflammation takes place when the temperature rises to about 70°. It also combines with sulphur,

$$P_4O_6 + 2S_2 = P_4O_6S_4.$$

Hydrogen chloride and phosphorus pentachloride give phosphorus trichloride as shown by the equations

$$P_4O_6 + 6HCl = 2PCl_3 + 2H_3PO_3$$
$$P_4O_6 + 6PCl_5 = 4PCl_3 + 6POCl_3.$$

* This would explain the fact that necrosis does not occur either in manufacture or when phosphorus is being charged into smoke-producing shells for military use, since in these cases the phosphorus is always wet and would give phosphorous acid instead of the volatile oxide.

The oxide inflames with absolute alcohol, the product (when the action is controlled) being a **diethyl phosphite** of the formula $(C_2H_5)_2HPO_3$.

(*c*) **Phosphorus dioxide**, $(PO_2)_n$.—When the preceding compound is heated in a sealed tube to 440° it decomposes into phosphorus dioxide and phosphorus (or a lower oxide of phosphorus),

$$P_4O_6 = 3PO_2 + P.$$

The dioxide can also be prepared by subliming, in a sealed tube at 290°, the mixture of oxides obtained by the slow combustion of phosphorus as in (*a*).

The dioxide sublimes in colourless crystals of density 2·5; the crystals are stable at 100°, but sublime when heated in a sealed tube at 180°. It dissolves slowly in water, giving an acid solution containing phosphorous and phosphoric acids.

In an attempt to determine the vapour density of the compound by Victor Meyer's method in a platinum apparatus no gas was liberated at 900°, although the compound usually sublimes at 180°; no importance can be attached therefore to the high vapour density recorded for the obviously altered product which was vaporised at 1400°.

(*d*) **Phosphoric oxide** or **phosphoric anhydride**, P_4O_{10}, can be prepared by burning phosphorus in air or oxygen. The action is strongly exothermic,

$$P_4 + 5O_2 = P_4O_{10} + 740{,}000 \text{ calories},$$

i.e., 74,000 calories are liberated for each atom of oxygen, as compared with

29,000	calories for	C		burning to	CO
67,000	,,	CO		,,	CO_2
68,360	,,	H_2		,,	H_2O
85,000	,,	Zn		,,	ZnO
100,000	,,	2Na		,,	Na_2O
and 127,000	,,	$\frac{2}{3}$Al		,,	$\frac{1}{3}Al_2O_3$.

The oxide is a colourless powder which can be purified by distillation over platinum in a current of oxygen. It dissolves in water with great liberation of heat, forming metaphosphoric acid, HPO_3, and then phosphoric acid, H_3PO_4,

$$P_4O_{10} + 6H_2O = 4H_3PO_4 + 70{,}000 \text{ calories}.$$

It is deliquescent, and is one of the best agents known for drying gases and liquids, or for the removal of the elements of water from compounds (see nitric anhydride, p. 416). Its vapour density at 1400° is a little higher than that required for the formula P_4O_{10}.

Hypophosphorous Acid and the Hypophosphites.

Salts of hypophosphorous acid, H_3PO_2, are obtained by the action of alkalies on phosphorus. In order to prepare the free acid, phosphorus is boiled with baryta water,

$$2P_4 + 3Ba(OH)_2 + 6H_2O = 2PH_3 + 3Ba(H_2PO_2)_2;$$

the acid is then set free by decomposing the barium salt with sulphuric acid. It is thus obtained as a syrup from which crystals, melting at 26·5°, can be obtained by evaporating under reduced pressure and freezing. When heated, the acid decomposes into phosphine and phosphoric acid (compare phosphorous acid). The acid is also oxidised to phosphoric acid by the action of chlorine and other oxidising agents, and is itself a powerful reducing agent, *e.g.*, it reduces mercuric chloride to mercurous chloride (compare phosphorous acid).

It is a monobasic acid and yields a series of HYPOPHOSPHITES of the type $M(H_2PO_2)$. **Sodium hypophosphite**, NaH_2PO_2, is used in medicine apparently with the idea that phosphorus in this form can be absorbed and utilised. The salts, like the free acid, are reducing agents and can be used to precipitate gold and silver from their salts.

Phosphorous Acid and the Phosphites. Hypophosphoric Acid.

Phosphorous acid, H_3PO_3, was first prepared by allowing moist phosphorus to smoulder in air. It is formed by the action of water on phosphorous oxide, and can be prepared in quantity by decomposing phosphorus trichloride with water and concentrating the liquid until it boils at 180°.

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

By the action of a further quantity of phosphorus trichloride **pyrophosphorous acid**, $H_4P_2O_5$ (*i.e.*, $2H_3PO_3 - H_2O$) is produced,

$$2PCl_3 + 5H_2O = H_4P_2O_5 + 6HCl.$$

The thick syrup formed in this way deposits in the first case crystals of phosphorous acid, H_3PO_3, melting at 70° C., and in the second case crystals of pyrophosphorous acid, $H_4P_2O_5$, melting at 38°.

When heated strongly, phosphorous acid (like hypophosphorous acid) gives phosphine and phosphoric acid,

$$4H_3PO_3 = PH_3 + 3H_3PO_4.$$

Phosphorous acid is also oxidised to phosphoric acid when exposed to air, or when used as a reducing agent to precipitate gold and silver from their solutions, or to reduce mercuric chloride to mercurous chloride or to mercury.

$$H_3PO_3 + 2HgCl_2 + H_2O = H_3PO_4 + Hg_2Cl_2 + 2HCl.$$

Phosphorous acid is a tribasic acid and forms PHOSPHITES of the type M_3PO_3, but usually only two of the three hydrogen atoms are replaced by metals. PYROPHOSPHITES, such as **sodium pyrophosphite**, $Na_4P_2O_5$, have also been prepared.

Hypophosphoric acid, $H_4P_2O_6$, is formed (with phosphorous acid) as the principal product of the smouldering of phosphorus. It is a tetrabasic acid and forms salts of four types, namely hydrates of

$$NaH_3P_2O_6 \quad Na_2H_2P_2O_6 \quad Na_3HP_2O_6 \quad Na_4P_2O_6.$$

The acid can be separated by preparing the **lead salt**, $Pb_2P_2O_6$, and decomposing this with hydrogen sulphide.

Phosphoric Acid and the Phosphates.

Phosphoric acid, H_3PO_4, is usually prepared by the action of sulphuric acid on calcium phosphate as described above (p. 419). Most of the gypsum is thrown out when the acid is concentrated, but the commercial acid may contain arsenic acid; this can be removed by reducing it to arsenious oxide by means of sulphurous acid, boiling to remove the excess of sulphur dioxide and then precipitating the arsenious oxide with hydrogen sulphide. Phosphoric acid is also formed by oxidising red phosphorus with nitric acid.

(*a*) **Orthophosphoric acid**, H_3PO_4.—Phosphoric acid exists in several forms containing different proportions of water; but, unlike the hydrates of sulphur trioxide, these are converted into one another only slowly and may even give different salts when neutralised. By evaporating the aqueous acid in a vacuum over sulphuric acid, the so-called **orthophosphoric acid**,* H_3PO_4, can be crystallised out in transparent prisms melting at 42°. It is a tribasic acid and forms three series of PHOSPHATES, *e.g.*,

Salt.	*Formula.*	*Reaction.*
Trisodium phosphate . . .	$Na_3PO_4,2H_2O$	Alkaline
Disodium hydrogen phosphate .	$Na_2HPO_4,12H_2O$	Neutral
Sodium dihydrogen phosphate .	NaH_2PO_4,H_2O	Acid

The first of these is strongly alkaline and is decomposed even by carbonic acid,

$$Na_3PO_4 + H_2O + CO_2 = Na_2HPO_4 + NaHCO_3.$$

The second is neutral to phenolphthalein, but alkaline to methyl-orange; with silver nitrate, however, it gives a strongly acid solution, owing to the partial precipitation of yellow trisilver phosphate,

$$Na_2HPO_4 + 3AgNO_3 \rightleftharpoons Ag_3PO_4 + 2NaNO_3 + HNO_3.$$

The third salt is acid to litmus but neutral to methyl-orange.

(*b*) **Pyrophosphoric acid**, $H_4P_2O_7$, prepared by heating phosphoric acid to 215°, may be regarded as an anhydride of the preceding acid,

$$2H_3PO_4 = H_4P_2O_7 + H_2O.$$

The acid melts at 61°; it does not at once revert to phosphoric acid when dissolved in cold water, but actually forms a hydrate with $1\frac{1}{2}H_2O$ which differs from the hydrates of phosphoric acid.

Pyrophosphoric acid forms a series of PYROPHOSPHATES which differ

* The term "ortho" is generally reserved for acids in which the whole of the oxygen is present as hydroxyl, as in orthosilicic acid, $Si(OH)_4$, or orthonitrous acid, $N(OH)_3$. Under this system, orthophosphoric acid should be $P(OH)_5$ and not $PO(OH)_3$.

from the orthophosphates in giving a *white* precipitate with silver nitrate, consisting presumably of **silver pyrophosphate**, $Ag_4P_2O_7$, and from the metaphosphates (see below) in not giving a precipitate with barium chloride or with albumen. They are prepared most readily by heating the mono-hydrogen phosphates; *e.g.*, **sodium pyrophosphate**, $Na_4P_2O_7$, is formed from disodium hydrogen phosphate,

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

Lead pyrophosphate, $Pb_2P_2O_7$, is prepared by adding lead acetate to a solution of the sodium salt; by precipitating the lead with sulphuretted hydrogen, a solution of pyrophosphoric acid is obtained, which is converted into orthophosphoric acid by boiling.

(*c*) **Metaphosphoric acid**, HPO_3, compare HNO_3, is obtained as a transparent, deliquescent glass, to which the name of GLACIAL PHOSPHORIC ACID is given, by igniting orthophosphoric acid. It volatilises at a bright red heat, and the appearance of a white fume is an indication that the removal of water from the phosphoric acid is complete. It is the first product formed when phosphoric oxide is exposed to moist air,

$$P_4O_{10} + 2H_2O = 4HPO_3,$$

but it is left behind when the oxide is resublimed. The acid is reconverted into ordinary phosphoric acid by boiling water and more slowly in the cold. Metaphosphoric acid differs from the ortho- and pyro-acids in giving white precipitates in solutions of calcium chloride, barium chloride, or albumen.

METAPHOSPHATES can be prepared either directly from the acid, or by heating the dihydrogen phosphates. Thus, **sodium metaphosphate,** $NaPO_3$, can be made by heating sodium dihydrogen phosphate,

$$NaH_2PO_4 = NaPO_3 + H_2O;$$

or microcosmic salt (p. 608),

$$Na(NH_4)HPO_4 = NaPO_3 + NH_3 + H_2O;$$

the product is a glass, which readily takes up metallic oxides when melted, forming coloured beads (compare borax beads, p. 584).

In addition to these simple salts, metaphosphates derived from polymeric acids, $(HPO_3)_n$, are known, where n may be 1, 2, 3, 4, or 6. These compounds differ from the periodates (p. 314) in that they are derived, not from a series of hydrates, but from acids of identical composition but of different molecular weight.

Perphosphoric Acids, H_3PO_5 and $H_4P_2O_8$.

The perphosphoric acids are closely analogous to the persulphuric acids (p. 348). They are formed by electrolysing slightly alkaline solutions of dipotassium phosphate, K_2HPO_4, containing also potassium fluoride, and a little potassium dichromate to prevent the reduction

at the cathode of the oxidised products formed at the anode. Two products are formed, namely,

(i) Salts of **per-*mono*-phosphoric acid**, H_3PO_5, which liberate iodine immediately from potassium iodide in presence of sulphuric acid, like Caro's per*mono*sulphuric acid, H_2SO_5, and are decomposed completely in alkaline solutions in the course of a few hours.

(ii) Salts of **per-*di*-phosphoric acid**, $H_4P_2O_8$, which liberate iodine much more slowly, like Marshall's per*di*sulphuric acid, $H_2S_2O_8$, and are remarkably stable even in solution, losing only 2 per cent. of available oxygen in the course of five days.

In the lower range of current density, per*di*phosphates are the main products, whilst at higher current densities per*mono*phosphates predominate, the total yield ranging from 70 per cent. downwards.

By careful evaporation on the water-bath, **tetrapotassium perphosphate**, $K_4P_2O_8$, can be isolated in fine crystals. It has an alkaline reaction, and does not oxidise potassium iodide ; after acidifying with acetic acid, however, there is a slow liberation of iodine on warming, and a more rapid oxidation when sulphuric acid is used. This salt may be regarded as the fourth member of a series which includes $K_4P_2O_5$, $K_4P_2O_6$, $K_4P_2O_7$, and $K_4P_2O_8$.

Phosphorus and the Halogens.

Simple Halogen-derivatives.

Phosphorus forms two principal series of halogen derivatives in which the element is tervalent and quinquevalent.

Phosphorus trifluoride, PF_3, prepared from arsenic trifluoride and phosphorus trichloride,

$$AsF_3 + PCl_3 = AsCl_3 + PF_3,$$

is a colourless gas condensing to a liquid which freezes at − 160° and boils at − 95°. It is more stable than the corresponding compounds with other halogens, since it does not fume in the air and is only slightly acted on by water.

Phosphorus pentafluoride, prepared by the action of arsenic trifluoride on phosphorus pentachloride,

$$5AsF_3 + 3PCl_5 = 5AsCl_3 + 3PF_5,$$

is a colourless gas, condensing to a liquid which freezes at − 83° and boils at − 75°. It is a stable compound, having the normal vapour density for the formula, PF_5 ; but it is partially dissociated into fluorine and the trifluoride by sparking.

Phosphorus trichloride, PCl_3, is formed by direct combination of chlorine with red or yellow phosphorus,

$$P_4 + 6Cl_2 = 4PCl_3.$$

In order to free the product from the pentachloride, it is digested with an excess of phosphorus and distilled.

Phosphorus trichloride is a mobile, colourless liquid of density 1·6. It boils at + 76° and freezes at − 112°. It has a pungent smell, and fumes in moist air. It is decomposed by water, giving hydrochloric and phosphorous acids,

$$PCl_3 + 3H_2O = 3HCl + H_3PO_3;$$

it is thus a convenient material for the preparation of phosphorous acid. It combines with chlorine to form a pentachloride, but will also dissolve phosphorus. It is used extensively in organic chemistry as an agent for replacing hydroxyl by chlorine, *e.g.*, in converting acetic acid into acetyl chloride,

$$\underset{\text{Acetic acid}}{3CH_3{\cdot}CO{\cdot}OH} + PCl_3 = \underset{\text{Acetyl chloride}}{3CH_3{\cdot}CO{\cdot}Cl} + \underset{\text{Phosphorous acid}}{H_3PO_3};$$

in this action it is converted into phosphorous acid, just as it is by the action of water.

Phosphorus pentachloride, PCl_5, is prepared by passing chlorine over the trichloride until it forms a dry solid,

$$PCl_3 + Cl_2 \rightleftarrows PCl_5 + 30{,}000 \text{ calories},$$

or by passing chlorine through a well-cooled solution of phosphorus in carbon disulphide and crystallising out the product. It forms yellowish-white crystals and melts under pressure at 148°.

When vaporised, phosphorus pentachloride dissociates partially into a mixture of phosphorus trichloride and chlorine; the vapour is therefore coloured by free chlorine, the presence of which can also be proved by allowing it to diffuse away in an atmosphere of carbon dioxide. The dissociation is endothermic and increases with rising temperature, becoming almost complete at 300°; but by vaporising the compound in an atmosphere of phosphorus trichloride dissociation can be prevented, and a normal vapour density is then observed.

EXERCISE.—From Cahours' figures for the vapour-density of phosphorus pentachloride deduce the percentage of dissociation at different temperatures.

Temperature .	182°	200°	250°	300°	336°
Density . . .	73·1	69·8	57·5	52·6	52·6

The calculated densities are, $H_2 = 1$, $Cl_2 = 35{\cdot}18$, $PCl_3 = 68{\cdot}15$, $PCl_5 = 103{\cdot}24$. The volumes compared with that of PCl_5 (density 103·24) are

Volume . . .	1·41	1·48	1·79	1·96	1·96

Since the volumes would be doubled by complete dissociation, the percentage of dissociation is as follows :—

Dissociation . .	41	48	79	96	96 per cent.

Phosphorus pentachloride fumes strongly in moist air and is

decomposed by water, giving the oxychloride, $POCl_3$, and then phosphoric acid, H_3PO_4.

$$PCl_5 + H_2O = POCl_3 + 2HCl$$
$$2POCl_3 + 6H_2O = 2H_3PO_4 + 6HCl.$$

It is used extensively as a more powerful agent than the trichloride for replacing oxygen or hydroxyl by chlorine, *e.g.*,

$$SO_3 + PCl_5 = SO_2Cl_2 + POCl_3.$$

Phosphorus tribromide, PBr_3, is prepared by mixing the elements in the presence of carbon disulphide or of benzene, or by carrying bromine vapour over phosphorus in a current of carbon dioxide in order to diminish the dangerous violence of the action. It is a colourless liquid, like the trichloride; it boils at 172° and freezes at − 41°. By further combination with bromine it yields yellow crystals of **phosphorus pentabromide**, PBr_5, melting at 106°. On exposure to light this gives deep red prisms, which are perhaps identical with the **heptabromide**, PBr_7, which is formed when bromine and the pentabromide are brought together in a sealed tube.

Phosphorus tri-iodide, PI_3, can be prepared by direct combination of red phosphorus with an excess of iodine in presence of carbon disulphide. It separates from solution in red crystals which melt at 61°. By using a smaller quantity of iodine, orange-red crystals of **diphosphorus tetraiodide**, P_2I_4, melting at 110°, are obtained. The vapour-density of the compound corresponds with the formula P_2I_4, compare P_2H_4.

Oxy-compounds.

Phosphorus oxychloride, $POCl_3$, is the first product of the action of water on phosphorus pentachloride,

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$

It is also formed by the action on phosphorus pentachloride of phosphoric oxide, or of oxalic acid, $H_2C_2O_4$,

$$PCl_5 + H_2C_2O_4 = POCl_3 + 2HCl + CO_2 + CO,$$

and by the oxidising action of potassium chlorate on the trichloride, PCl_3,

$$KClO_3 + 3PCl_3 = 3POCl_3 + KCl.$$

It is a colourless, fuming liquid of density 1·7, which boils at 108° and freezes to a solid at 1°.

Phosphorus oxyfluoride, POF_3, is a gas (boiling-point − 40°), and **phosphorus oxybromide**, $POBr_3$, is a solid (melting-point + 55°).

PHOSPHORUS AND SULPHUR.

Sulphides of Phosphorus.

Phosphorus (melting-point 44°) and sulphur (melting-point 114°) form an eutectic mixture containing 23 per cent. of sulphur, and freezing

at + 10° ; but this condition is unstable, and combination between the two elements soon takes place. The freezing-point curve (Fig. 171) then shows the presence of the following compounds :

Formula.	*Melting-point.*
PS_6	314°
P_2S_5	290°
P_2S_3	296°
P_4S_3	172°

together with a sulphide richer in phosphorus, which is perhaps P_2S.

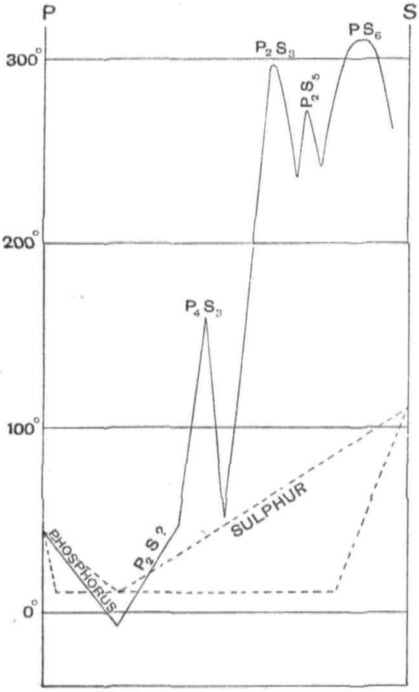


FIG. 171.—FREEZING-POINT CURVES FOR PHOSPHORUS AND SULPHUR.

Two of these compounds are commercial products, and are sufficiently stable to be crystallised from solution ; thus, P_2S_5 separates from carbon disulphide in yellow crystals and boils at 515°, and P_4S_3 separates from carbon disulphide or from phosphorus trichloride in rhombic crystals and boils at 408° ; the former compound is used as a reagent in organic chemistry for replacing oxygen by sulphur and the latter as a substitute for phosphorus in the manufacture of matches.

PHOSPHORUS AND NITROGEN.

Nitrogen Compounds.

A number of compounds containing the univalent AMINO-group, $-NH_2$, the bivalent IMINO-group, $=NH$, the tervalent radical $\equiv N$ are known,

(i) P_2S_5 and NH_3 at a red heat give the quinquevalent nitride P_3N_5.

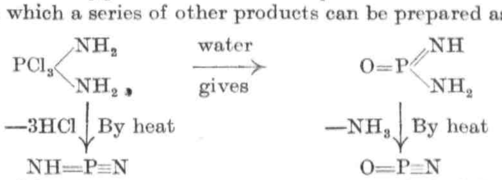
(ii) P_2O_5 and NH_3 when slightly moist appear to give acids of the type

$$O{=}P{\begin{matrix}\diagup OH\\ -OH\\ \diagdown NH_2\end{matrix}} \quad \text{and} \quad O{=}P{\begin{matrix}\diagup OH\\ -NH_2\\ \diagdown NH_2\end{matrix}}$$

(dibasic) (monobasic)

These can be prepared in a pure state from their organic derivatives.

(iii) PCl_5 and NH_3 give a mixture of $2NH_4Cl$ and the diamine $PCl_3(NH_2)_2$ from which a series of other products can be prepared as follows :—



" *Phospham* " " *Phosphoryl nitride* "

Detection and Estimation of Phosphorus.

Phosphorus is usually detected and estimated in the form of phosphoric acid. This gives with silver nitrate, in neutral or feebly acid solutions, a white or yellow **silver phosphate**, Ag_3PO_4, and with a solution of ammonium molybdate in nitric acid a canary-yellow precipitate of **ammonium phosphomolybdate,** $(NH_4)_3PO_4,10MoO_3$. It can be precipitated in a crystalline form as **ammonium magnesium phosphate,** $(NH_4)MgPO_4,6H_2O$, and is usually estimated in this form ; the precipitate can be weighed as such, dried to the anhydrous salt, or ignited and weighed as **magnesium pyrophosphate**, $Mg_2P_2O_7$; or it may be dissolved in an excess of standard hydrochloric acid and the excess titrated with standard sodium hydroxide, using as an indicator methyl-orange, which gives a neutral indication with ammonium dihydrogen phosphate,

$$(NH_4)MgPO_4 + 2HCl = MgCl_2 + (NH_4)H_2PO_4.$$

The atomic weight of phosphorus has been determined from the ratio P : 5Ag by precipitating silver from silver sulphate by weighed quantities of phosphorus.

CHAPTER XXVIII

6. CARBON. C = 12·00.

Occurrence of Carbon.

(*a*) *Carbonates.*—Carbon is only a minor constituent (about 0·2 per cent. of the outer 10 miles) of the earth's crust. Like phosphorus it is found in igneous rocks to the extent of 0·13 per cent., in an elementary form as DIAMOND and GRAPHITE and in combination as CANCRINITE, $3NaAlSiO_4,NaHCO_3$, a mineral which must obviously have crystallised out under pressure. It is, however, an important constituent of sedimentary rocks, where immense quantities of carbonates are found, *e.g.*, as CHALK or LIMESTONE, $CaCO_3$, DOLOMITE, $CaMg(CO_3)_2$, SPATHIC IRON ORE, $FeCO_3$, etc. These carbonates are products of the decomposition of silicates, from which the metals have been dissolved out in the form of soluble bicarbonates, *e.g.*, $Mg(CO_3H)_2$, $Ca(CO_3H)_2$, $Fe(CO_3H)_2$, and precipitated again in the form of insoluble carbonates. Many of the industrial metals are also found in the form of carbonates, *e.g.*, $ZnCO_3$, $PbCO_3$, etc.; but these have usually been formed as secondary products by the action of atmospheric carbon dioxide on the original sulphide ores of metalliferous veins.

(*b*) *Carbon Dioxide.*—Uncombined carbon dioxide is present in the atmosphere to the extent of about 3 parts in 10,000 by volume, and this proportion is apparently kept constant by equilibrium with the bicarbonates in sea-water. The total amount of carbon dioxide in the air corresponds with a layer of carbon over the earth's surface only 1 mm. in thickness and is only 1/30,000 of that present in sedimentary rocks; it is an interesting speculation whether, prior to the disintegration of igneous rocks, the whole of this carbon dioxide was present in the atmosphere, increasing its mass about 15-fold, or whether it was held as graphite or as cancrinite in molten rocks.

(*c*) *Organic Compounds.*—All plant and animal tissues contain a large proportion of carbon, which has been separated by reduction from atmospheric carbon dioxide; this element is therefore of fundamental importance both in the animal and in the vegetable kingdom. In combination with hydrogen and oxygen, and to a smaller extent with nitrogen, sulphur, phosphorus, and the metals, it has yielded, in Nature and in the laboratory, so many compounds as to constitute a separate branch of chemistry under the name of ORGANIC CHEMISTRY. The

principal feature of these compounds is the presence of long chains and rings of carbon atoms. Thus, ordinary FAT has the formula $C_{57}H_{110}O_6$, and contains 3 chains of 18 carbon atoms linked through oxygen to a central nucleus of glycerine containing a short chain of 3 carbon atoms. COTTON and STARCH, $(C_6H_{10}O_5)_n$, are complex compounds built up from units which contain chains of 6 carbon atoms; and compounds containing carbon and hydrogen only are known which contain uninterrupted chains of carbon atoms up to $C_{60}H_{122}$. These compounds are quite stable even when containing very large numbers of atoms, perhaps because the volume of the carbon atom is smaller than that of any other element, *e.g.*, 12 grams of diamond occupy only 3·4 c.c., whereas 28·3 grams of silicon, containing the same number of atoms, occupy 12 c.c.

(*d*) *Coal and Oil.*—Vegetable matter, largely deprived of its hydrogen and containing a high proportion of carbon, is found in horizontal seams of COAL, which forms the principal source of heat and power at the present time. By distilling wood and coal, inflammable gases and TAR are driven out, and a solid residue of CHARCOAL or COKE remains. The carbon deposited on the walls of the retort by further decomposition of the volatile products is known as GAS CARBON, whilst the carbon left behind in the form of soot by burning oil in an insufficient supply of air is known as LAMPBLACK.

Natural hydrocarbons, in the form of MINERAL OIL or PETROLEUM, are of increasing importance as fuel for the supply of power. The more volatile fractions can be exploded directly with air in internal combustion engines, whilst the crude oil and the less volatile fractions are burnt by explosion in Diesel and Ackroyd engines, or as LIQUID FUEL in the form of spray under boilers in conjunction with steam engines or turbines. The principal GASEOUS FUELS are described below (p. 464).

(*e*) *Elementary Carbon* is found in Nature in two distinct forms, namely, in a quasimetallic form as GRAPHITE and in a transparent non-metallic form as DIAMOND (see below).

ELEMENTARY CARBON.

The Allotropy of Carbon.

Carbon exists in three allotropic forms, as charcoal, graphite, and diamond, and was the first element in which the phenomenon of allotropy (p. 81) was recognised. Graphite and diamond are crystalline substances of definite composition, but charcoal is a crude product which is very difficult to purify, except under conditions which cause it to change into graphite.

Charcoal.

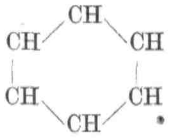
(*a*) *Preparation.*—Charcoal is prepared either by the partial combustion of wood or by dry distillation in closed retorts, when various

by-products (wood-spirit, acetone, acetic acid, wood-tar) are also obtained. The product is a complex material containing carbon, hydrogen, and oxygen, in addition to considerable quantities of mineral matter. If prepared at a sufficiently high temperature, the greater part of the oxygen can be driven out in combination with hydrogen and carbon; but the presence of hydrogen can still be proved by passing chlorine over it at a high temperature, when hydrogen chloride escapes; this process also serves to purify the charcoal, so that it can be obtained practically free both from hydrogen and from chlorine.

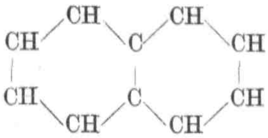
(*b*) *Physical Properties.*—Charcoal is a porous material, which has a very large surface relatively to its weight; it floats on water, since its apparent density is only about 0·25, although the real density of the carbon is about 1·9. It has a remarkable power of condensing gases, especially when it has been "activated" by heating for long periods at high temperatures. At low temperatures its absorptive power is still more remarkable; thus, charcoal made from cocoa-nut shells, when cooled with liquid air, will condense every gas but hydrogen, neon, and helium, producing almost a perfect vacuum; at this temperature it will condense oxygen so quickly that liquid oxygen can be made to freeze by its own rapid evaporation. When cooled with liquid hydrogen, charcoal will condense every gas but helium, and was used by Onnes to purify the helium used for liquefaction, in order to prevent the apparatus from freezing up with solid air or hydrogen.

(*c*) *Chemical Properties.*—Charcoal is the most active form of carbon, its heat of combustion being 96,960 calories for 12 grams as compared with 94,810 calories for graphite and 94,310 calories for diamond. It ignites in oxygen a little above 400°, whereas graphite does not burn until about 700°, and diamond at about 800°. Again, charcoal ignites at once in fluorine at atmospheric temperatures, whilst graphite burns only at 500°, and diamond at 700°.

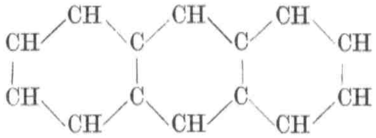
(*d*) *Constitution.*—When charcoal is boiled with fuming nitric acid for twenty-four hours, and then oxidised further by adding potassium chlorate to the boiling solution, organic acids are produced which can be precipitated as barium salts and then converted into ammonium salts, giving a yield of about 25 per cent. of ammonium mellitate. The same yield is obtained from charcoal containing 2 per cent. or only 0·2 per cent. of hydrogen, but coal (which has been carbonised by slow oxidation at low temperatures) gives very little mellitic acid. **Mellitic acid,** $C_{12}H_6O_{12}$, is a derivative of benzene, C_6H_6, and contains a ring of six carbon atoms to each of which a univalent carboxyl group, —CO·OH, is attached, so that it may be written as $C_6(CO_2H)_6$. This ring of six carbon atoms is familiar, not only in **benzene**, C_6H_6, the most volatile of the hydrocarbons in coal-tar, but also in the fractions of higher boiling-point, such as **naphthalene**, $C_{10}H_8$, which contains two such rings, and **anthracene**, $C_{14}H_{10}$, which contains three rings:



Benzene



Naphthalene



Anthracene

The production of mellitic acid by oxidation of charcoal can be accounted for by assuming the presence of a hexagonal network of carbon atoms as in Fig. 172, which shows the network needed to produce one molecule of mellitic acid.

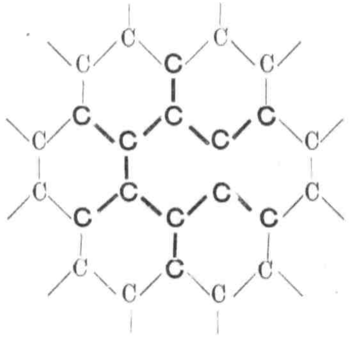


FIG. 172.—MOLECULAR STRUCTURE OF CHARCOAL.

In these ring-compounds the carbon acts as if it were tervalent instead of quadrivalent, but the boundary of the network must be fringed with hydrogen atoms. By heating the charcoal more strongly, the hydrogen is gradually eliminated as the ring-system becomes more complex. This elimination is facilitated by the presence of chlorine; but when brought to completion by heating to a high temperature it results in a complete conversion of charcoal into graphite. Examination by *X*-rays has, however, shown that ordinary charcoal already contains crystalline material having the same structure as graphite.

Graphite.

(*a*) *Occurrence.*—GRAPHITE or PLUMBAGO was formerly found as a black, lustrous mineral in Cumberland, and is still used there in the manufacture of " blacklead " pencils. It is now obtained chiefly from Ceylon, the United States, and Madagascar. It is occasionally found in

igneous rocks as a primary crystallisation from the liquid magma, but appears much more frequently in metamorphic rocks, where a carbonaceous sediment has been carried down and recrystallised at high temperatures and pressures. Natural graphite usually contains from 3 to 5 per cent. of ash, but may be purified by extracting it with potash and with hydrochloric acid.

(b) *Preparation.*—Graphite may be produced artificially by the crystallisation of carbon from cast iron. The carbon usually separates first in the form of a **carbide of iron,** Fe_3C, but decomposes into iron and graphite on prolonged annealing; in presence of silicon, the carbide of iron is less stable and graphite is usually formed instead. Iron which contains its carbon in the form of carbide is known as "white cast

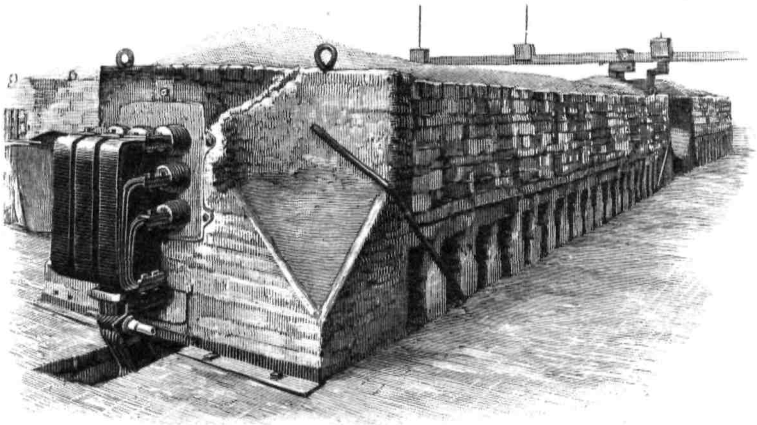


FIG. 173.—ELECTRIC FURNACE FOR THE MANUFACTURE OF GRAPHITE.

iron"; that which contains it in the form of graphite is called "grey cast iron."

Graphite is manufactured on a very large scale at Niagara by heating anthracite in an electric furnace (Fig. 173, compare Fig. 187). Not only does the carbon become crystalline, but the mineral matter is distilled out of it, so that the product contains less than 0·1 per cent. of impurity.

Physical Properties of Graphite.

(a) *Density, Softness, and Lustre.*—Graphite forms well-defined hexagonal crystals of density 2·25. Its most remarkable property is its extreme softness, which makes it of great value as a lubricant; thus, under a pressure of about 50 atmospheres it will flow like a liquid. In the absence of acids, pure artificial graphite will remain suspended indefinitely in water containing small quantities of organic matter, or in oil, and in this form is of special value in lubricating the

bearings of heavy machinery. On account of its softness and blackness, graphite is used in the manufacture of pencils, whilst its softness, permanence in air, and semi-metallic lustre have led to its use in the form of " black lead " for polishing iron.

(*b*) *Electrical Conductivity.*—Unlike the diamond, graphite possesses marked electrical conductivity; the resistance between opposite faces of a centimetre cube is, however, about one-hundredth of an ohm, as compared with one- or two-millionths of an ohm for copper. On account of its relatively high resistance, blocks of carbon, pressed together by means of a screw, are used as a variable resistance when working with electric currents of moderate size, whilst a spiral cut from a block of artificial graphite, and carrying a heavy current, affords a very convenient method of heating a furnace which is required to work in the highest ranges of temperature.

(*c*) *Vaporisation.*—When graphite is heated to the temperature of the electric arc, it vaporises without melting. On account of its high boiling-point, graphite electrodes are used to lead the current into electric furnaces working at high temperatures, *e.g.*, in the manufacture of graphite, carborundum (p. 488), and calcium carbide (p 626). The conductivity of carbon vapour is made use of in the ELECTRIC ARC, in which the current is carried by carbon vapour between a pair of carbon electrodes. The life of the carbons may be increased by using an " enclosed arc " shielded by an inner globe of glass in order to check the combustion of the carbon. The intensity of the light is augmented greatly by using a core of mineral matter (usually cerium fluoride) in the carbons; the arc then becomes charged with metallic vapours, which increase both its brilliancy and its conductivity, so that the length of a " flame arc " may be increased from the fraction of an inch to several inches.

Chemical Properties of Graphite.

(*a*) *Stability.*—The *heat of combustion* of graphite is slightly larger than that of diamond, suggesting that the diamond is the more stable form of the element. In practice, however, the diamond can be converted into graphite by heating it, whilst the converse change has not yet been effected by any simple process. Thus the greater density of the diamond suggests that its production from graphite would be easier if the pressure were increased; but this anticipation has not been verified, and graphite appears to be perfectly stable over the whole range of temperatures and pressures that have been reached in experiments on this subject.

(*b*) *Resistance to Oxidation and Chlorination.*—When heated in air or oxygen, graphite burns to carbon dioxide, but the combustion is so slow that, when mixed with fireclay as a " binder," it can be used for the manufacture of crucibles. Graphite is also very resistant to attack by chlorine and is therefore generally used as the anode when chlorine is

liberated by electrolysis. When, however, oxygen is liberated at the anode, the carbon is consumed rapidly, and cheaper materials, such as "gas carbon," are commonly used instead of graphite.

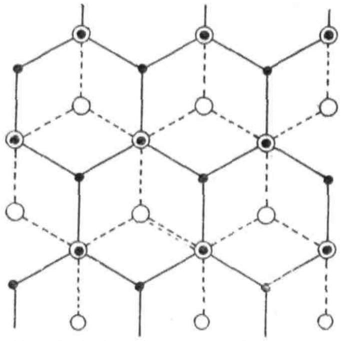


FIG. 174.—STRUCTURE OF GRAPHITE.

(c) *Constitution.* — When oxidised at a low temperature by a mixture of potassium chlorate and nitric acid, graphite is converted into a complex yellow compound, known as **graphitic acid**, which by further treatment is broken down into mellitic acid. Graphite has, therefore, the same complex hexagonal ring-system as well-burnt charcoal. This ring-system is also shown in the structure of the crystals as determined by examination with *X*-rays and reproduced in Fig. 174.

Occurrence and Preparation of the Diamond.

(*a*) The main source of diamonds at the present time is the "blue earth" of South Africa. This is a decomposed igneous rock found in conical pipes (Fig. 175) which are believed to represent the necks of extinct volcanoes. Diamonds up to 621 grams in weight have been discovered in the "blue earth," although it only contains about 1 part in 10 million of crystalline carbon. The diamonds are believed to have crystallised out from a lava or magma consisting mainly of magnesium silicates. This view has been confirmed—

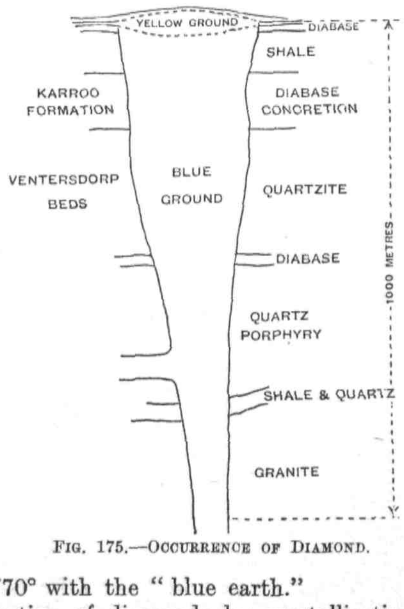


FIG. 175.—OCCURRENCE OF DIAMOND.

(i) By the discovery of diamonds in meteoric stones of similar composition to the "blue earth."

(ii) By the fact that diamonds are corroded by heating to 1770° with the "blue earth."

(iii) By the artificial production of diamonds by crystallisation from magnesium silicate and from molten olivine, a mineral consisting mainly of magnesium silicate.

(*b*) Diamonds have also been detected in meteoric iron and have been prepared artificially by Moissan by quenching solutions of carbon in molten iron or silver. As the diamond is about 50 per cent. denser than graphite, it was thought that the high pressure produced by the quenching was responsible for the separation of diamonds in place of graphite, but it has not been found possible to convert graphite into diamond by pressure alone, even at the highest attainable temperatures. The thermo-chemical data indicate that the diamond should be slightly more stable than graphite, but the difference in the heats of combustion is very small, and the general behaviour of the diamond resembles that of a metastable substance which can only be persuaded to crystallise out by a trick, *e.g.*, by separation from a particular solvent.

Properties of the Diamond.

(*a*) *Crystalline Form.*—The diamond crystallises in the cubic system, and well-developed octahedra are occasionally found (Fig. 176); these are believed to be twin-crystals built up from two tetrahedra (p. 210). It has a series of cleavage planes, parallel to the octahedral faces, which are made use of in shaping rough diamonds; edges produced by cleavage are also used in cutting glass. The structure of the crystals, as established by investigation with *X*-rays, has been shown in Fig. 101, p. 218, where each carbon atom is situated at the centre of gravity of four other atoms, occupying the corners of a regular tetrahedron or triangular pyramid. In this arrangement, therefore, all the carbon is definitely quadrivalent, as in the saturated compounds of the "fatty series," of which marsh gas, CH_4, may be taken as the type. In graphite, on the other hand, the carbon appears to be arranged in hexagonal rings as in the "aromatic compounds," of which benzene, C_6H_6, is the type.

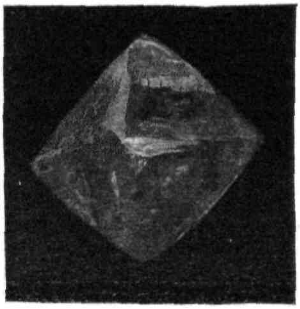


FIG. 176.—OCTAHEDRAL CRYSTAL OF DIAMOND.

(*b*) *Hardness.*—Diamond is the hardest of known crystals and cannot be scratched by any other mineral; it must therefore be polished by using diamond-dust as an abrasive. Its extreme hardness adds much to its value as a gem-stone, since the facets will retain their polish where a softer crystal would quickly become scratched and dull. The great hardness of the diamond may perhaps be associated with the perfect symmetry in every direction of the lattice work of the crystal, whilst the extreme softness of graphite may be attributed to the presence of "gliding planes" parallel to the hexagonal network.

(*c*) *Density and Refractive Index.*—Diamond has a density of 3·5

as compared with 2·25 for graphite. Its refractive index is 2·42, and is responsible for the extreme brilliance of cut diamonds, since most of the light which enters the stone is "totally reflected" from the interior surfaces even although it strikes these at quite a steep angle.

(*d*) *Oxidation.*—Diamonds when burnt in air are oxidised to carbon dioxide, but, unlike charcoal and graphite, they do not yield any intermediate products of oxidation.

Chemical Properties of Carbon.

(*a*) *Combination with the Non-metals.*—Carbon is a very inactive element. When heated, it burns in air or oxygen to **carbon dioxide,** CO_2, but this action can be arrested by careful drying; when almost completely dry it may burn slowly to **carbon monoxide,** CO. It also combines with sulphur-vapour to form **carbon disulphide**, CS_2. It combines directly with fluorine, but chlorine, bromine, iodine, and nitrogen have no action upon it. A number of compounds of carbon with hydrogen can be formed by direct combination of the two elements, but these are usually produced only in very small proportions.

(*b*) *Combination with Metals.*—Carbon combines with a few of the metals to form CARBIDES. The carbides of the more active metals, such as **calcium carbide**, CaC_2, and **aluminium carbide,** Al_4C_3, are *decomposed by water.* *With iron, carbon may form either a solid* solution, to which the name of AUSTENITE is given, or a **carbide**, Fe_3C, to which the name of CEMENTITE is given. With manganese, it forms a corresponding **manganese carbide,** Mn_3C, but with nickel it gives only an eutectic mixture. No carbides are formed in the case of copper, silver and gold, zinc, cadmium and mercury, tin and lead, arsenic, antimony, and bismuth; this is an important factor in facilitating the use of carbon as a reducing agent in metallurgy, whilst, on the other hand, the formation of calcium carbide serves to prevent the preparation of calcium by the direct reduction of lime.

CARBON AND HYDROGEN.

Hydrocarbons and Carbohydrates.

The name HYDROCARBON is applied to compounds which contain carbon and hydrogen only; the term CARBOHYDRATE is used to describe those compounds which contain carbon, hydrogen, and oxygen in such quantities that if the carbon were removed the hydrogen and oxygen would be in the right proportions to form water, *e.g.*:

Hydrocarbons.		*Carbohydrates.*	
Methane . . .	CH_4	Formaldehyde . .	CH_2O
Ethane . . .	C_2H_6	Grape-sugar . . .	$C_6H_{12}O_6$
Ethylene . . .	C_2H_4	Cane-sugar . . .	$C_{12}H_{22}O_{11}$
Acetylene . . .	C_2H_2	Cellulose and starches	$(C_6H_{10}O_5)_n$
Benzene . . .	C_6H_6		
Naphthalene . .	$C_{10}H_8$		

Methane or Marsh Gas, CH_4.

(*a*) *Preparation.*—The " inflammable air of marshes " was examined in 1772 by Volta, who collected it by stirring up the mud near the shores of some of the Italian lakes, and showed that it required for its combustion a much larger volume of air than was necessary in the case of hydrogen. Marsh gas may be prepared

(i) By heating dry sodium acetate with four times its weight of soda-lime (*i.e.*, quicklime slaked with caustic soda),

$$CH_3\cdot CO\cdot ONa + NaOH = Na_2CO_3 + CH_4.$$

The gas is passed through concentrated sulphuric acid to absorb any ethylene that may be produced and is collected over water, in which it is almost insoluble. A small amount of hydrogen is always present in the gas.

(ii) By reducing methyl iodide, CH_3I (dissolved in methyl alcohol), with a moist zinc-copper couple, *i.e.*, zinc rendered active by immersion in a dilute solution of copper sulphate,

$$CH_3I + 2H = CH_4 + HI.$$

By reduction with sodium, ethane, C_2H_6 (p. 449), the next homologue of methane, is produced,

$$2CH_3I + 2Na = C_2H_6 + 2NaI.$$

(iii) By the action of water on aluminium carbide,

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4.$$

(iv) By passing a mixture of sulphuretted hydrogen and the vapour of carbon disulphide over red-hot copper,

$$CS_2 + 2H_2S + 8Cu = CH_4 + \underset{\text{Cuprous sulphide}}{4Cu_2S}.$$

(*b*) *Balanced Actions giving rise to Methane.*—Methane is formed by the direct combination of carbon with hydrogen, but only at temperatures so high as to produce almost complete decomposition, *e.g.*, at 1400°, when only 0·8 per cent. of methane is produced. The equilibrium at lower temperatures, as determined from experiments on the decomposition of methane, is as follows :

TABLE 49.—FORMATION AND DISSOCIATION OF METHANE.

	$C + 2H_2$	$\rightleftarrows$	CH_4 + 21,700 calories
At 400° .	14 %		86 %
600° . .	68		32
800° . .	96		4
1000° . .	99		1

As the combination of carbon and hydrogen is accompanied by a decrease of volume, it is facilitated by increased pressure, and under a pressure of 150 atmospheres the equilibrium-mixture at 1400° contains 20 per

cent. instead of 0·8 per cent. by volume of methane. As the temperature is raised the methane is accompanied by increasing quantities of acetylene; thus at 2500° and atmospheric pressure the equilibrium-mixture contains about 1 per cent. of methane and 3·5 per cent. of acetylene.

Methane is also produced by the interaction of carbon monoxide and hydrogen as follows:

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \text{ (vapour)} + 50{,}700 \text{ calories.}$$

This action is even more strongly exothermic than the direct combination of carbon with hydrogen, and is therefore favoured very greatly by reducing the temperature of reaction, *e.g.*, by catalysis with nickel at 250–300°, when even minute traces of carbon monoxide can be eliminated from hydrogen by conversion to methane. At 800°, on the other hand, the action would proceed almost completely in the opposite direction.

(*c*) *Physical Properties.*—Methane is a colourless, odourless gas which condenses to a liquid boiling at − 160° and freezing at −184°. At 0° and atmospheric pressure, 100 c.c. of water dissolves 5·5 c.c. of methane.

(*d*) *Chemical Properties.*—Methane contains a single atom of quadrivalent carbon, the chemical affinity of which is completely SATURATED by four atoms of hydrogen. It is a very inactive compound, forming no addition compounds, although the hydrogen can be replaced by chlorine or by oxygen. It is the simplest member of an important HOMOLOGOUS SERIES, *i.e.*, of a series of compounds differing by increments of $—CH_2—$. The compounds of this series are known as the PARAFFINS on account of their chemical inactivity; they can all be represented by the general formula C_nH_{2n+2}, and the series can therefore be extended beyond methane to include hydrogen ($n = 0$). The chemical properties of methane are as follows:

(i) By prolonged sparking methane is decomposed into carbon and hydrogen (Dalton),

$$\underset{1\ vol.}{CH_4} = C + \underset{2\ vols.}{2H_2}$$

(ii) Methane burns with a non-luminous flame to carbon dioxide and water, and forms an explosive mixture with air when more than 5·3 per cent. of methane is present. The "fire-damp" of coal mines consists of methane, and the "after-damp" of an explosion owes its poisonous properties to carbon monoxide formed by incomplete oxidation of methane, as shown in the equation

$$2CH_4 + 3O_2 = 2CO + 4H_2O.$$

When exploded with excess of oxygen, methane uses up two volumes of this gas and yields its own volume of carbon dioxide,

$$\underset{1\ vol.}{CH_4} + \underset{2\ vols.}{2O_2} = \underset{1\ vol.}{CO_2} + 2H_2O.$$

(iii) By the action of chlorine in sunlight, hydrogen may be displaced atom by atom giving rise to a series of SUBSTITUTION PRODUCTS.

$$CH_4 + Cl_2 = HCl + CH_3Cl \text{ (methyl chloride)}$$
$$CH_3Cl + Cl_2 = HCl + CH_2Cl_2 \text{ (methylene chloride)}$$
$$CH_2Cl_2 + Cl_2 = HCl + CHCl_3 \text{ (chloroform)}$$
$$CHCl_3 + Cl_2 = HCl + CCl_4 \text{ (carbon tetrachloride)}$$

(iv) Chemical agents, such as strong nitric acid, alkaline potassium permanganate, bromine water, and strong sulphuric acid, have no action on methane.

Ethane, C_2H_6.

Ethane is the next homologue of methane in the paraffin-series. It may be prepared

(i) By the action of sodium on methyl iodide (p. 447),

$$2CH_3I + 2Na = C_2H_6 + 2NaI.$$

(ii) By the action of a zinc-copper couple on a mixture of ethyl iodide and ethyl alcohol,

$$C_2H_5I + 2H = C_2H_6 + HI.$$

(iii) By passing a mixture of ethylene (see below) and hydrogen over finely-divided nickel at 450° (Sabatier),

$$C_2H_4 + H_2 = C_2H_6.$$

Ethane resembles methane very closely, but has a higher density, a higher boiling-point at − 93°, and a higher freezing-point at − 171° ; water dissolves about 10 per cent. of the gas at 0°, as compared with 5·5 per cent. of methane.

Ethylene or **Olefiant Gas,** C_2H_4.

This compound is the first member of a series of hydrocarbons, the OLEFINES, of the general formula C_nH_{2n}, containing two atoms of hydrogen less than the corresponding paraffins.

(*a*) *Preparation.*—Ethylene is prepared by removing a molecule of water from ethyl alcohol,

$$C_2H_6O = C_2H_4 + H_2O$$

This can be effected by the action

(i) of strong sulphuric acid at 180.
(ii) of syrupy phosphoric acid at 230°, or
(iii) of alumina at about 450°.

Ethylene can also be separated from coal-gas by absorption in charcoal, and experiments have been made with a view to converting this gas into alcohol by combination with water.

(*b*) *Physical Properties.*—Ethylene is a colourless gas which dissolves more readily in water, and is more easily liquefied than the two gaseous

paraffins described above. Water at 0° dissolves 23 per cent. of its volume of the gas. The liquid boils at − 103° and freezes at − 169°.

(c) *Chemical Properties.*

(i) Ethylene (like methane) is decomposed by prolonged sparking, depositing carbon and liberating twice its volume of hydrogen.

$$\underset{1\ vol.}{C_2H_4} = 2C + \underset{2\ vols.}{2H_2}$$

(ii) Ethylene burns with a luminous flame and contributes largely to the luminosity of coal-gas. When exploded with excess of oxygen, it uses three volumes of this gas and liberates two volumes of carbon dioxide, whilst methane uses two volumes of oxygen and gives one volume of carbon dioxide.

$$\underset{1\ vol.}{C_2H_4} + \underset{3\ vols.}{3O_2} = \underset{2\ vols.}{2CO_2} + 2H_2O.$$

$$\underset{1\ vol.}{CH_4} + \underset{2\ vols.}{2O_2} = \underset{1\ vol.}{CO_2} + 2H_2O.$$

(iii) Ethylene, which contains two atoms of hydrogen less than ethane, is an UNSATURATED COMPOUND and forms ADDITION COMPOUNDS with H_2, Cl_2, Br_2, HCl, HBr, HOCl, H_2SO_4, etc. The oily compound **ethylene dichloride** or DUTCH LIQUID, $C_2H_4Cl_2$, which is formed by the combination of ethylene with an equal volume of chlorine,

$$C_2H_4 + Cl_2 = C_2H_4Cl_2,$$

provided the first test for recognising this gas, and gave to it its name of OLEFIANT GAS (*i.e.*, oil-forming gas). The compound of ethylene with sulphur dichloride,

$$2C_2H_4 + SCl_2 = S(C_2H_4Cl)_2,$$

is commonly known as MUSTARD GAS. Ethylene also combines with fuming sulphuric acid, forming **ethyl hydrogen sulphate** or "sulphovinic acid,"

$$C_2H_4 + H_2SO_4 = C_2H_5{\cdot}HSO_4,$$

from which, on diluting with water and distilling, ethyl alcohol can be recovered,

$$C_2H_5{\cdot}HSO_4 + H_2O = C_2H_5OH + H_2SO_4.$$

Acetylene, C_2H_2.

(a) *Preparation.*

(i) Acetylene is produced in small quantities by the direct combination of hydrogen and carbon in the electric arc or by passing hydrogen over carbon heated to 2500°,

$$2C + \underset{1\ vol.}{H_2} \rightleftharpoons \underset{1\ vol.}{C_2H_2}.$$

(ii) It is produced on a large scale by the action of water on calcium carbide, CaC_2 (p. 626),

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

(*b*) *Physical Properties.*—Acetylene is a colourless gas, the characteristic odour of which is due to impurities, *e.g.*, phosphoretted hydrogen formed by the action of water on calcium phosphide (derived from calcium phosphate in the chalk used for making the carbide).

It condenses to a colourless liquid which boils at $-81°$ and freezes at $-84°$. At atmospheric temperatures, it condenses to a liquid under a pressure of 40 atmospheres at 20°, but is then liable to explode spontaneously; it can, however, be transported safely in iron cylinders when dissolved under pressure in acetone in presence of some porous material.

(*c*) *Chemical Properties.*

(i) Acetylene burns with a very smoky flame, but gives a brilliant light when two jets of the gas impinge to form a thin flat flame. When burnt with an excess of oxygen in a blowpipe, it produces a very hot flame, which can be used for welding cracks in iron, for burning rivet-holes in steel rails or plates, and even for cutting armour-plate.

(ii) Acetylene is an unsaturated compound and combines with $2H_2$, $2Cl_2$, $2Br_2$, etc. On passing the gas into dilute sulphuric acid, in which mercuric oxide is held in suspension by vigorous stirring, it unites with water to form **acetaldehyde,*** C_2H_4O,

$$C_2H_2 + H_2O = CH_3{\cdot}CHO,$$

from which synthetic **acetic acid**, $CH_3{\cdot}CO{\cdot}OH$, is prepared on a large scale by atmospheric oxidation, *e.g.*, in presence of manganese acetate at 25 to 40°.

(iii) The hydrogen of acetylene may be replaced by metals, with the formation of ACETYLIDES. Thus **silver acetylide**, C_2Ag_2, is formed as a white powder by passing acetylene through an ammoniacal solution of silver nitrate; in the same way, **cuprous acetylide**, C_2Cu_2,H_2O, is formed as a red precipitate by leading acetylene into an ammoniacal solution of a cuprous salt; it loses its water when dried at 100°; both compounds are very explosive. **Sodium acetylide**, C_2HNa, is prepared most readily by the action of acetylene on a solution of sodium in liquid ammonia (p. 381),

$$2NH_3Na + 2C_2H_2 = C_2HNa + NaNH_2 + C_2H_4 + NH_3.$$

Benzene, C_6H_6.

This hydrocarbon, which has the same composition as acetylene, but a higher molecular weight, is the parent substance from which the natural and artificial AROMATIC COMPOUNDS are derived. It can be separated from coal-tar by fractional distillation and is also an

* Aldehyde = alcohol dehydrogenatum, C_2H_6O minus H_2.

important constituent of Borneo petroleum. It is formed by a process of polymerisation when acetylene is passed through a red-hot tube,

$$3C_2H_2 = C_6H_6.$$

Benzene is a colourless liquid with a characteristic odour; it is insoluble in water, but mixes with most organic liquids, and is frequently used as a solvent for resins and fats. It boils at 80·2° and melts at 5·6°. It burns with a smoky, luminous flame. When acted on by nitric acid, one or more hydrogen atoms are replaced by univalent nitro-groups, $—NO_2$, *e.g.*,

$$C_6H_6 + HNO_3 = \underset{\text{Nitrobenzene}}{C_6H_5{\cdot}NO_2} + H_2O,$$

whilst when treated with fuming sulphuric acid one or more hydrogen atoms are replaced by the sulphonic acid group, $—SO_3H$, *e.g.*,

$$C_6H_6 + H_2SO_4 = \underset{\text{Benzenesulphonic acid.}}{C_6H_5{\cdot}SO_3H} + H_2O.$$

HALOGEN-DERIVATIVES OF CARBON.

Derivatives of Methane.

Carbon tetrachloride, CCl_4, cannot be prepared from its elements by direct combination, since chlorine does not act on carbon. It is therefore made by the action of chlorine or of sulphur chloride on carbon disulphide; in the former case, antimony pentachloride is used as a " carrier " of chlorine,

$$CS_2 + 2Cl_2 = CCl_4 + S_2$$
$$CS_2 + 2S_2Cl_2 = CCl_4 + 3S_2.$$

It is a volatile, fragrant liquid, insoluble in water, and boiling at 77°. It contains more than 90 per cent. of chlorine, and is of special value as a non-inflammable solvent; it is also used extensively as a fire extinguisher. It has been used as a hair-wash, but is very dangerous, as it is more toxic than chloroform and has been known to produce fatal effects.

Chloroform, $CHCl_3$, prepared by the action of bleaching powder on alcohol, is a heavy, fragrant liquid, of density 1·50 at 15°, freezing at − 63° and boiling at + 61°. It is used very largely as an anæsthetic, its efficiency in this respect being increased by the presence, in chloroform made from alcohol, of a little ethyl chloride, C_2H_5Cl (p. 453.)

Iodoform, CHI_3, prepared in a similar way to chloroform by the action of iodine and sodium carbonate on alcohol, is a yellow crystalline solid of density 4·0, with a pungent and characteristic odour, melting at 119°, which is used extensively as an antiseptic.

Carbonyl chloride or **phosgene,** $COCl_2$, was prepared by Davy by the action of sunlight on a mixture of carbon monoxide and chlorine,

$$CO + Cl_2 \rightleftharpoons COCl_2,$$

and can be prepared on a large scale by using charcoal as a catalyst (p. 462). It is also formed by the oxidising action of air on chloroform, in which it may appear as a poisonous impurity,

$$2CHCl_3 + O_2 = 2COCl_2 + 2HCl;$$

chloroform for use as an anæsthetic should therefore be stored in full bottles, closely stoppered and in the dark. A convenient method of preparation is by the oxidising action on carbon tetrachloride of fuming sulphuric acid (p. 340),

$$2SO_3 + CCl_4 = COCl_2 + S_2O_5Cl_2.$$

Phosgene is a colourless gas which condenses readily to a liquid; this boils at 8° and freezes at − 127°. The gas fumes in moist air owing to the formation of hydrochloric acid,

$$COCl_2 + H_2O = CO_2 + 2HCl.$$

With alcohol, it gives **ethyl chlorocarbonate**, $Cl{\cdot}CO{\cdot}OC_2H_5$, which by the action of ammonia is converted into **urethane** or **ethyl carbamate**, $NH_2{\cdot}CO{\cdot}OC_2H_5$, compare ammonium carbamate, $NH_2{\cdot}CO{\cdot}ONH_4$ (p. 604); carbamic acid, $NH_2{\cdot}CO{\cdot}OH$, is, however, still unknown.

Derivatives of Ethane.

Ethyl chloride, C_2H_5Cl, the first product of the action of chlorine on ethane,

$$C_2H_6 + Cl_2 = C_2H_5Cl + HCl,$$

is prepared by the action of hydrogen chloride on alcohol in the presence of zinc chloride,

$$C_2H_5{\cdot}OH + HCl = C_2H_5Cl + H_2O.$$

It is a colourless, fragrant gas which burns with a green flame. It condenses readily to a liquid boiling at 14°; owing to the cold produced by its evaporation, this liquid is used as a local anæsthetic and in ice-making machines.

Ethylene dichloride, $C_2H_4Cl_2$, prepared by the direct combination of ethylene with chlorine (p. 450), is a fragrant liquid boiling at 84°, whilst **ethylene bromide,** $C_2H_4Br_2$, melts at 10° and boils at 129°.

Acetylene tetrachloride, $C_2H_2Cl_4$, prepared by the direct combination of acetylene with chlorine,

$$C_2H_2 + 2Cl_2 = C_2H_2Cl_4,$$

resembles ethylene dichloride, but boils at 147°.

Dicarbon hexachloride, C_2Cl_6, was prepared by Faraday (1824) by the further action of chlorine in sunlight on ethylene dichloride,

$$C_2H_4Cl_2 + 4Cl_2 = C_2Cl_6 + 4HCl.$$

It is a crystalline solid with a camphor-like odour, and melts at 187°.

Addition and Substitution of Chlorine.

The four preceding compounds may be regarded as SUBSTITUTION PRODUCTS formed by replacement of hydrogen by chlorine in ethane, C_2H_6. From this point of view they may be described as follows:

Ethyl chloride or monochloroethane, C_2H_5Cl
Ethylene chloride or dichloroethane, $C_2H_4Cl_2$
Acetylene tetrachloride or tetrachloroethane, $C_2H_2Cl_4$
Dicarbon hexachloride or hexachloroethane, C_2Cl_6.

Further chlorination results finally in a separation of the two carbon atoms,

$$C_2Cl_6 + Cl_2 = 2CCl_4,$$

which is difficult to effect in any other way except by burning, *i.e.*, by complete oxidation of the parent hydrocarbon. The prefix " chloro " implies that chlorine has displaced hydrogen from the parent substance, whilst the term " chloride " is used to describe the addition of chlorine to ethylene or to acetylene, or (hypothetically) to carbon in the hexachloride, C_2Cl_6.

CARBON AND OXYGEN.

Oxides of Carbon.

The chief oxides of carbon are

Carbon dioxide, or carbonic anhydride, CO_2.
Carbon monoxide, or carbonic oxide, CO.

In addition, the anhydrides of some organic acids may be included amongst the oxides of carbon, since they consist of carbon and oxygen only, *e.g.*,

$$\underset{\text{Malonic acid}}{CH_2(COOH)_2} - 2H_2O = \underset{\text{Carbon suboxide}}{C_3O_2}$$

$$\underset{\text{Mellitic acid}}{C_6(COOH)_6} - 3H_2O = \underset{\text{Mellitic anhydride}}{C_{12}O_9}.$$

Attention may also be directed to the existence of PERCARBONATES (p. 459), *e.g.*, $K_2C_2O_6$, with a higher state of oxidation than in carbon dioxide.

Carbon Dioxide, CO_2.

The existence of a poisonous GAS SYLVESTRE was recognised by Van Helmont (1577–1644) in the fumes from a charcoal fire, as a product of the fermentation of wine, and in the suffocating gases of the Grotto del Cani; but it was not until 1755 that Black established by definite chemical tests the presence in chalk and the alkalies of a FIXED AIR which was driven off when chalk was burnt to lime, and which escaped

with effervescence when these substances were acted on by acids. The physical properties of the gas, including its density and its solubility in water, were examined and measured by Cavendish in 1766.

Preparation of Carbon Dioxide.

(*a*) *By the Action of Acids on Carbonates.*—Carbon dioxide is usually prepared in the laboratory by the action of hydrochloric acid on marble (compare the apparatus shown in Fig. 104, p. 222),

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

For making aerated water, sulphuric acid was used with "whiting" (*i.e.*, soft chalk) or sodium bicarbonate,

$$CaCO_3 + H_2SO_4 = CaSO_4 + CO_2 + H_2O$$
$$2NaHCO_3 + H_2SO_4 = Na_2SO_4 + 2CO_2 + 2H_2O.$$

(*b*) *By Fermentation.*—The first aerated waters were made by Priestley by exposing water to the gas in the vats in which beer was being brewed; large quantities of this gas are now collected, compressed into cylinders, and supplied to makers of aerated waters.

(*c*) *By Combustion.*—Carbon dioxide is made industrially by burning coke in air, passing the gases through water to absorb sulphur dioxide, and absorbing the carbon dioxide in aqueous potassium carbonate; by boiling this solution the carbon dioxide is liberated in a concentrated form, and is compressed into cylinders after drying with sulphuric acid,

$$K_2CO_3 + H_2O + CO_2 \underset{\text{hot}}{\overset{\text{cold}}{\rightleftarrows}} 2KHCO_3$$

The steel cylinders in which the gas is sent out usually contain about $\frac{1}{2}$ cwt. of carbon dioxide, in a liquid form, under a vapour-pressure of about 60 atmospheres.

(*d*) *By Burning Limestone.*—The very large quantities of carbon dioxide required for making sodium carbonate by the Solvay process (p. 571) are made by burning a mixture of limestone and coke in a kiln (Fig. 177) provided with an artificial draught,

$$C + O_2 = CO_2; \quad CaCO_3 = CaO + CO_2.$$

The kiln (Fig. 177) is an iron shell lined with fire-bricks and supported on iron columns. It is charged with alternate layers of coke (about 10 per cent.) and limestone (about 90 per cent.), and brought to redness by opening the cover *A* of the central chimney during the early stages of combustion; the temperature of the charge is judged by viewing it through mica-windows as at *aa*. The cover is then closed and the gases are drawn out through the pipe *B* by means of a suction-pump. Fresh lime and coke are introduced through a conical hopper by lifting up the cylindrical collar *C*, and the lime and ashes are raked out from the base of the cone *D*. The gas on its way to the pump is purified by passing through a trap *E* to remove

condensed water and dust. It is not practicable to use steam to facilitate the liberation of carbon dioxide from combination with lime, since this sets

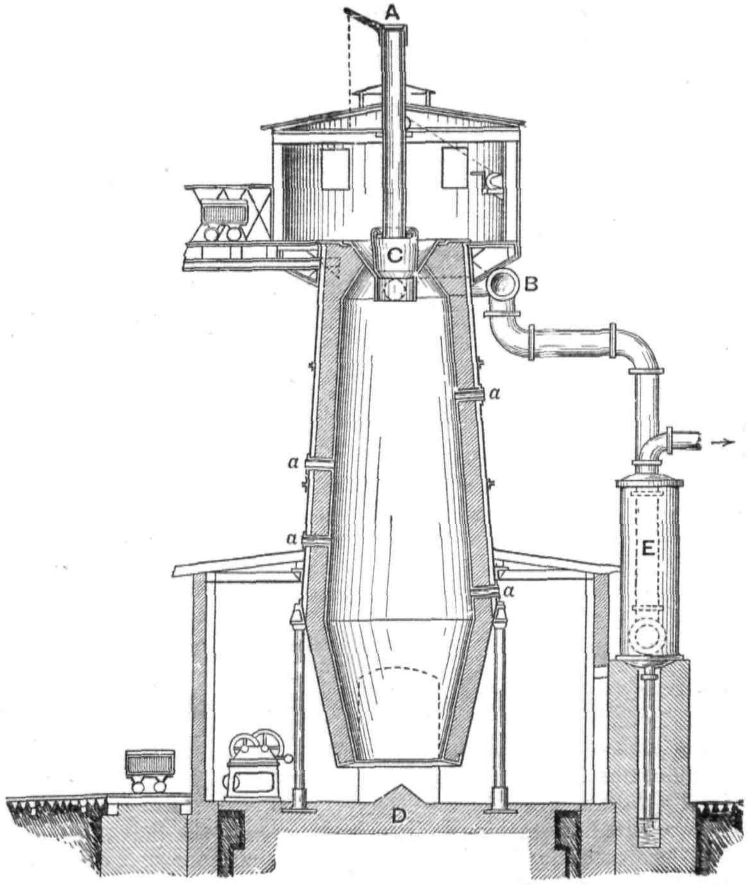


FIG. 177.—LIME-KILN FOR MANUFACTURE OF CARBON DIOXIDE. (After Lunge.)

free hydrogen sulphide from calcium sulphide formed by reduction of calcium sulphate in the limestone. The gantry used to elevate the trucks is not shown in the figure.

Physical Properties of Carbon Dioxide.

The close resemblance between the physical properties of nitrous oxide, N_2O, and carbon dioxide, CO_2, has already been shown in Table 46, p. 410. The general properties of the dioxide are set out below.

(*a*) *Density.*—Carbon dioxide is a colourless gas with a density of nearly 2 grams per litre at 0° and 760 mm. pressure.

(*b*) *Liquid and Solid Carbon Dioxide.*—At the critical pressure of

31° carbon dioxide can be liquefied under a critical pressure of 73 atmospheres. At 15°, the vapour pressure of the liquid is 52 atmospheres falling to 34 atmospheres at 0°, and to 5·1 atmospheres at − 56·7°, when the liquid freezes. The vapour pressure of the solid falls to one atmosphere at − 79°; this is therefore the "sublimation-point," corresponding with the "boiling-point" of a liquid, at which the solid vaporises under atmospheric pressure. Liquid carbon dioxide cannot be preserved under atmospheric pressure, but is converted at once into the solid; CARBON DIOXIDE SNOW may therefore be collected by inverting a cylinder of the compressed gas and allowing the liquid to escape from the nozzle into a muslin bag. It can be used, either alone or mixed into a paste with ether or acetone, as a convenient means of cooling to − 79°.

(*c*) *Carbon Dioxide and Water.*—Carbon dioxide dissolves in an equal volume of water at 15° (Cavendish, 1766), but the whole of the gas is expelled by boiling and nearly all of it is lost on exposure to air. The solubility is much greater when the pressure is increased; water is therefore frequently used to remove carbon dioxide from compressed gases, and may also be employed as a means of concentrating and purifying carbon dioxide.

Chemical Properties of Carbon Dioxide.

(*a*) *Volumetric Relationships.*—Carbon burns to carbon dioxide without any marked change in volume (Priestley, Lavoisier, 1772),

$$\underset{}{C} + \underset{1\ vol.}{O_2} = \underset{1\ vol.}{CO_2}$$

When reduced to the monoxide by means of carbon, its volume is doubled,

$$\underset{}{C} + \underset{1\ vol.}{CO_2} = \underset{2\ vols.}{2CO}$$

(*b*) *Reduction.*—Carbon dioxide can be reduced to the monoxide by the action of carbon at a high temperature either upon the free gas or upon a carbonate, such as chalk or barium carbonate,

$$BaCO_3 + C = BaO + 2CO.$$

Reduction to carbon monoxide can also be brought about by metals such as iron acting either on chalk or on the gas (see below, p. 460).

A partial reduction to carbon can be effected at a red heat by the action of sodium, potassium, or magnesium on the gas,

$$4K + 3CO_2 = 2K_2CO_3 + C,$$

or of phosphorus-vapour on chalk,

$$6CaCO_3 + P_4 = \underset{\text{Calcium phosphate}}{2Ca_3(PO_4)_2} + 2CO + 4C$$

(*c*) *Dissociation.*—When carbon dioxide is heated strongly it dissociates into carbon monoxide and oxygen. The observed proportions

of these gases when equilibrium is reached at different temperatures are approximately as follows :

TABLE 50.—DISSOCIATION OF CARBON DIOXIDE.

	$2CO_2$	$\rightleftharpoons$	$2CO + O_2$.
At 1200° . . .	99·98%		0·02%
At 2000° . . .	98		2
At 2600° . . .	50		50

(*d*) *Addition.*—Carbon dioxide unites with water to form carbonic acid, with basic oxides to form carbonates, with hydroxides to form bicarbonates, and with ammonia to form ammonium carbamate (p. 459).

Carbonic Acid and its Derivatives.

(*a*) *Carbonic Acid.*—A solution of carbon dioxide in water has a slight acid taste, which is attributed to the presence in it of small quantities of **carbonic acid**, H_2CO_3,

$$CO_2 + H_2O \rightleftharpoons H_2CO_3.$$

The solution is not acid to methyl-orange, but it produces a dull red tint with litmus, which reverts to a blue colour when the solution is boiled. The acid gives two series of salts, namely, CARBONATES, such as K_2CO_3 and $CaCO_3$, in which both atoms of hydrogen are replaced by metal, and BICARBONATES, in which only half the hydrogen is displaced, as in $KHCO_3$ and $Ca(CO_3H)_2$.

(*b*) *Carbonates* are produced by direct combination of carbon dioxide with basic oxides in the presence of a trace of moisture,

$$CaO + CO_2 = CaCO_3,$$

by displacement of water from hydroxides,

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$
$$2KOH + CO_2 = K_2CO_3 + H_2O,$$

or by double decomposition

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl.$$

The carbonates of the alkalies, *e.g.* Na_2CO_3, give an immediate precipitate when added to solutions of magnesium sulphate or of mercuric chloride, whereas the bicarbonates, *e.g.* $NaHCO_3$, give a precipitate only when the solution is boiled.

(*c*) *Bicarbonates* may be produced by direct combination of carbon dioxide with hydroxides,

$$KOH + CO_2 = KHCO_3,$$

by the solvent action of carbonic acid on insoluble carbonates or silicates (pp. 438 and 511), *e.g.*,

$$CaCO_3 + H_2CO_3 = \underset{\text{Calcium bicarbonate}}{Ca(CO_3H)_2},$$

and by dissolving metals such as iron or zinc in carbonic acid,

$$Fe + 2H_2CO_3 = \underset{\text{Ferrous bicarbonate}}{Fe(CO_3H)_2} + H_2.$$

It is noteworthy that whilst the bicarbonates of the alkalies are less soluble than the carbonates, the alkaline earths which form insoluble carbonates give rise to soluble bicarbonates.

(*d*) *Percarbonates.*—When a solution of potassium carbonate is electrolysed at $-30°$ to $-40°$, it gives **potassium percarbonate**, $K_2C_2O_6$, as a bluish-white, deliquescent, amorphous powder,

$$2K_2CO_3 = 2K + (CO_3K)_2;$$

compare potassium persulphate,

$$2K_2SO_4 = 2K + (SO_4K)_2.$$

The percarbonate can be regarded as a derivative of hydrogen peroxide

$$\begin{array}{l} O\cdot CO\cdot OK \\ | \\ O\cdot CO\cdot OK \end{array}, \quad \text{compare} \quad \begin{array}{l} O\cdot SO_2\cdot OK \\ | \\ O\cdot SO_2\cdot OK. \end{array}$$

It is a strong oxidising and bleaching agent, liberates iodine from potassium iodide,

$$K_2C_2O_6 + 2KI = 2K_2CO_3 + I_2,$$

and when heated decomposes into potassium carbonate, carbon dioxide, and oxygen.

(*e*) *Carbonates, Carbamates, and Carbamide.*—With ammonia and water, carbon dioxide forms **ammonium carbonate**, $(NH_4)_2CO_3$; compare Na_2CO_3.

$$2NH_3 + CO_2 + H_2O = CO(ONH_4)_2 \text{ (ammonium carbonate).}$$

Carbon dioxide also combines directly with ammonia to form **ammonium carbamate**, $(NH_3)_2CO_2$, a compound which can be derived from the carbonate by removing a molecule of water,

$$2NH_3 + CO_2 = NH_2\cdot CO\cdot ONH_4 \text{ (ammonium carbamate).}$$

Carbamide or **urea**, $CO(NH_2)_2$, the principal nitrogenous constituent of urine, is the " amide " of carbonic acid, containing $2NH_2$ instead of $2OH$; it therefore contains 1 molecule of water less than ammonium carbamate and 2 molecules of water less than ammonium carbonate. It is readily hydrolysed by acids or alkalies, or by the action of a ferment or enzyme to which the name of UREASE is given, giving rise to ammonium carbonate (or products from its further decomposition), as shown in the equation

$$CO(NH_2)_2 + 2H_2O = CO(ONH_4)_2.$$

(*f*) *Carbonyl chloride* or *phosgene*, $COCl_2$ (p. 452), is the " acid chloride " of carbonic acid, $CO(OH)_2$, since it can be derived from

it by replacing the two hydroxyls by chlorine, and is converted into carbamide, $CO(NH_2)_2$, by the action of ammonia.

Detection and Estimation of Carbon Dioxide.

Carbon dioxide is usually detected by its power of precipitating chalk from lime-water. It can be estimated gravimetrically by absorption in a strong solution of potash (p. 367) or volumetrically by titration (see Pettenkofer's method for CO_2 in air, p. 367). Bicarbonates behave as neutral salts when titrated with phenolphthalein, but as alkalies when methyl-orange is used; the temporary hardness of water (p. 632) can therefore be determined by direct titration of the soluble bicarbonates against an acid with methyl-orange as indicator.

Preparation of Carbonic Oxide or Carbon Monoxide, CO.

(*a*) *By Oxidation of Carbon.*—Carbon cannot, as a rule, be burnt directly to carbon monoxide by means of air or oxygen, but this partial oxidation can be effected by oxides which are not readily reduced, including both water and carbon dioxide, *e.g.*,

$$ZnO + C = CO + Zn$$
$$H_2O + C = CO + H_2 \text{ (see “ water gas,” p. 468)}$$
$$CO_2 + C = 2CO \text{ (see “ producer gas,” p. 467).}$$

Direct oxidation of carbon to carbon monoxide may also take place when charcoal is heated in oxygen under conditions of almost perfect dryness.

(*b*) *By Reduction of Carbon Dioxide.*—Carbon monoxide may be prepared by reducing carbon dioxide or a carbonate by means of carbon or a metal,

$$CO_2 + C = 2CO$$
$$BaCO_3 + C = 2CO + BaO$$
$$4CaCO_3 + 3Fe = 4CO + 4CaO + Fe_3O_4.$$

(*c*) *By the Action of Sulphuric Acid on Formic Acid, Oxalic Acid, or Potassium Ferrocyanide.*

$$\underset{\text{Formic acid}}{H{\cdot}CO{\cdot}OH} = H_2O + CO$$
$$\underset{\text{Oxalic acid}}{H_2C_2O_4} = H_2O + CO + CO_2$$
$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 6CO + 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4.$$

The last is a curious action, in which water is added to a cyanide by the action of concentrated sulphuric acid; it should be noted, however, that the cyanide is converted into basic products, including ammonia, for which sulphuric acid has even more affinity than for water.

(*d*) *Commercial Manufacture.*—Gaseous fuels containing carbon monoxide are prepared by the action of air and steam on coke or coal

(see below, p. 467), but these products are complex mixtures from which carbon monoxide cannot readily be isolated. Carbon monoxide containing only a small proportion of impurities can be prepared on a large scale by passing carbon dioxide over charcoal at temperatures above 1000°, but this method is not easy to carry out on account of the large amount of heat that must be supplied to the charcoal. It can also be prepared by passing oxygen into charcoal, when carbon dioxide is formed, and then reduced to the monoxide by the further action of charcoal on the hot gas; but in this action so much heat is liberated that it is difficult to maintain the plant. The ideal method of preparation is therefore to pass into a gas producer, charged with charcoal, a mixture of carbon dioxide and oxygen in such proportions as to maintain a convenient working temperature in the producer.

Physical Properties of Carbon Monoxide.

Carbon monoxide is a colourless gas, which is fourteen times heavier than hydrogen, and almost exactly equal in density to nitrogen, which it resembles in its physical properties just as carbon dioxide resembles nitrous oxide (p. 550 and Table 46, p. 410). It forms a colourless liquid boiling at − 190°, and a snow-like solid melting at − 200°. It is only *slightly soluble* in water, which dissolves only 3 per cent. of its volume of the gas at 8° as compared with 2 per cent. of nitrogen or hydrogen, 4 per cent. of oxygen, and 6 per cent. of nitric oxide.

TABLE 51.—PHYSICAL PROPERTIES OF NITROGEN AND CARBONIC OXIDE.

	N_2	CO		N_2	CO
Freezing-point . .	− 210°	− 200°	Density of liquid at boiling-point	0·796	0·793
Boiling-point . .	− 196°	− 190°	Solubility of gas in water at 8°, by volume . .	2	3%
Critical temperature	− 146°	− 140°	Viscosity of gas at 0°, $\times 10^6$ . .	166	163
Critical pressure .	35	36 atm.			
Critical volume .	5·17 c.c.	5·05 c.c.			

Chemical Properties of Carbon Monoxide.

Carbon monoxide, containing 1 atom of oxygen less than the dioxide, is an unsaturated compound, and nearly all its reactions depend on the formation of addition-compounds, thus:

(*a*) *Oxidation.*—Carbon monoxide burns with a blue flame, uniting with half its volume of oxygen to produce an equal volume of carbon dioxide,

$$\underset{2\ vols.}{2CO} + \underset{1\ vol.}{O_2} = \underset{2\ vols.}{2CO_2}$$

This action, which is reversed at very high temperatures, is retarded greatly even by the very partial drying that can be produced by means of sulphuric acid ; it has therefore been suggested that the combustion takes place in two stages, hydrogen being first produced (perhaps as a product of decomposition of formic acid) and then burnt to water, as follows :

$$CO + H_2O = \underset{\text{Formic acid}}{H_2CO_2} = H_2 + CO_2.$$

$$2H_2 + O_2 = 2H_2O.$$

In presence of finely-divided nickel or platinum at temperatures from 300° upwards, carbon monoxide decomposes into carbon and carbon dioxide. At high temperatures, however, carbon monoxide is more stable than carbon dioxide (compare Dissociation of Carbon Dioxide, p. 458). This is shown clearly in the following table.

TABLE 52.—DISSOCIATION OF CARBONIC OXIDE.

$$2CO \rightleftharpoons C + CO_2 + 39{,}000 \text{ calories.}$$

Temperature .	500°	600°	700°	800°	900°	1000°
CO_2 in gas . .	95	77	42	7	2·2	0·6%

On account of its ready oxidation, carbon monoxide is a powerful reducing agent, and is capable of removing oxygen from many metallic oxides, *e.g.*,

$$CuO + CO = CO_2 + Cu.$$

It is, however, a less powerful reducing agent than carbon and is not able to remove oxygen from refractory oxides such as zinc oxide ; it is for this reason that these oxides give rise to carbon monoxide rather than to carbon dioxide when reduced by means of carbon.

Carbon monoxide reduces (and is oxidised by) Fehling's solution (p. 839), an ammoniacal solution of silver nitrate, an aqueous solution of palladious chloride, and warm iodine pentoxide. A mixture of metallic oxides has also been discovered which will oxidise carbon monoxide to carbon dioxide at atmospheric temperatures.

(*b*) *Combination with Chlorine.*—In the presence of sunlight or of an active form of charcoal, carbon monoxide unites directly with an equal volume of chlorine to form carbonyl chloride (p. 452). This is an exothermic balanced action, in which the proportion of carbonyl chloride diminishes as the temperature rises, thus :

TABLE 53.—FORMATION AND DISSOCIATION OF CARBONYL CHLORIDE.

	$CO + Cl_2$	$\rightleftharpoons COCl_2 + 26{,}140$ calories.
At 300°	4%	96%
At 400°	20	80
At 500°	55	45

The presence of a catalyst which will promote combination at low

temperatures is therefore essential for securing a good yield of the chloride.

(c) *Absorption by Alkalies.*—Carbon monoxide can be absorbed by sodium hydroxide (*e.g.*, in the form of soda-lime) to produce sodium formate,

$$CO + NaOH = H{\cdot}CO{\cdot}ONa.$$

This is a reversal of the action which takes place in the presence of sulphuric acid.

(d) *Combination with Metals.*—Carbon monoxide unites directly with certain metals to form METALLIC CARBONYLS which are readily decomposed again by heat. The most important of these is **nickel carbonyl**, $Ni(CO)_4$, which is used in the Mond process for separating and purifying nickel (p. 806). An explosive **potassium carbonyl**, $K_6(CO)_6$, formed by combination of carbon monoxide with potassium, has been shown to be a derivative of benzene, namely, $C_6(OK)_6$, compare benzene, C_6H_6, and mellitic acid, $C_6(CO_2H)_6$.

(e) *Absorption by Cuprous Chloride.*—Carbon monoxide is readily absorbed by acid or ammoniacal solutions of cuprous chloride, which may absorb as much as twenty times their volume of the gas. The absorption is due to chemical combination, as a very unstable crystalline solid has been isolated, which probably has the formula $Cu_2Cl_2,CO,2H_2O$.

(f) *Physiological Action of Carbon Monoxide.*—Carbon monoxide is extremely poisonous. A violent headache is brought about by breathing air containing 1 part in 40,000 of carbon monoxide. Air containing 1 part in 1000 gradually produces unconsciousness and then death, while air containing 1 per cent. of carbon monoxide causes death in about two minutes. The gas combines with the hæmoglobin of the blood to form a bright red substance having a characteristic absorption spectrum. Normal blood slowly turns brown when exposed to the atmosphere, but blood containing carbon monoxide retains its bright red colour during several months.

(g) *Detection and Estimation.*—Carbon monoxide may be identified by the blue colour of its flame and by the formation of carbon dioxide as the only product of combustion. Small quantities of carbon monoxide in air may be detected by shaking with diluted blood, and then examining the blood either spectroscopically, or by adding a solution of tannin to it, when normal blood gives a brown precipitate, whilst blood containing carbon monoxide gives a red precipitate.

Carbon monoxide may be estimated by absorbing it in ammoniacal cuprous chloride, after removing hydrocarbons, carbon dioxide, and oxygen. Traces of carbon monoxide in air may be determined by passing it through tubes containing iodine pentoxide heated to 160°, when the following action takes place:

$$5CO + I_2O_5 = 5CO_2 + I_2;$$

the iodine is absorbed in bulbs containing potassium iodide and is estimated by titration.

Thermochemical Data.

The data in reference to the oxides of carbon are as follows:

	C (charcoal)	+	O_2	=	CO_2	+ 96,960 calories
	CO	+	$\frac{1}{2}O_2$	=	CO_2	+ 67,960 calories
∴	C (charcoal)	+	$\frac{1}{2}O_2$	=	CO	+ 29,000 calories

compare:

H_2	+	$\frac{1}{2}O_2$	=	H_2O (liquid)	+ 68,360 calories
H_2	+	$\frac{1}{2}O_2$	=	H_2O (gas)	+ 58,000 calories

The heat of combustion of charcoal is 96,960 calories, and that of carbon monoxide is 67,960 calories; it follows that the heat of formation of carbon monoxide from charcoal is 96,960 — 67,960 = 29,000 calories. The small value of the heat of formation of carbon monoxide from charcoal as compared with the heat of formation of carbon dioxide from carbon monoxide may be explained by assuming that in the combustion of charcoal a large amount of energy is used up in breaking down the complex molecules of carbon into atoms, which are then converted into carbon monoxide. The thermochemical data suggest that carbon monoxide should be a more powerful reducing agent than carbon; the actual greater effectiveness of carbon may be attributed to its high boiling-point, which fixes it, so that it can only escape after oxidation to the monoxide or dioxide.

Carbon monoxide and hydrogen, which behave in a very similar manner as reducing agents, are seen to have very similar heats of combustion. The equilibrium-constant in the equation

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

becomes equal to unity at 830°. Below this temperature the reduction of steam by carbon monoxide predominates over the reduction of carbon dioxide by hydrogen, so that carbon monoxide is the more powerful reducing agent; thus, carbon monoxide reduces iodine pentoxide, I_2O_5, at 160°, cupric oxide at 75°, and yellow mercuric oxide at 0°; whereas hydrogen only begins to reduce the two metallic oxides at temperatures 50° higher. Above 830°, the conditions are reversed and hydrogen is the more efficient reducing agent.

Gaseous, Liquid, and Solid Fuels

Gaseous Fuels.

(*a*) **Natural Gas**, the simplest and richest of all gaseous fuels, is a mixture consisting principally of methane, *e.g.*, CH_4, 60 to 90 per cent., with smaller proportions of hydrogen, H_2, and ethane, C_2H_6.

(*b*) **Coal Gas**, prepared by distilling coal in fireclay retorts, consists principally of hydrogen and methane, *e.g.*,

Composition of Coal Gas	H_2	CH_4	C_2H_4	CO	CO_2	N_2
	48	32	4	8	2	6 %

A residue of COKE is left in the retorts, whilst the liquid products include

(i) An aqueous AMMONIACAL LIQUOR from which ammonia is distilled out into sulphuric acid and converted into ammonium sulphate.

(ii) COAL TAR, from which benzene, C_6H_6, toluene, C_7H_8, naphthalene, $C_{10}H_8$, anthracene, $C_{14}H_{10}$, and pitch are separated by fractional distillation, after removing *acids* such as carbolic acid, or phenol, C_6H_5OH, by washing with alkalies, and *bases* such as pyridine, C_5H_5N, by washing with sulphuric acid.

The retorts are made of fireclay 3 inches thick, about 20 inches wide and 13 inches high internally. They are commonly arranged in lengths of

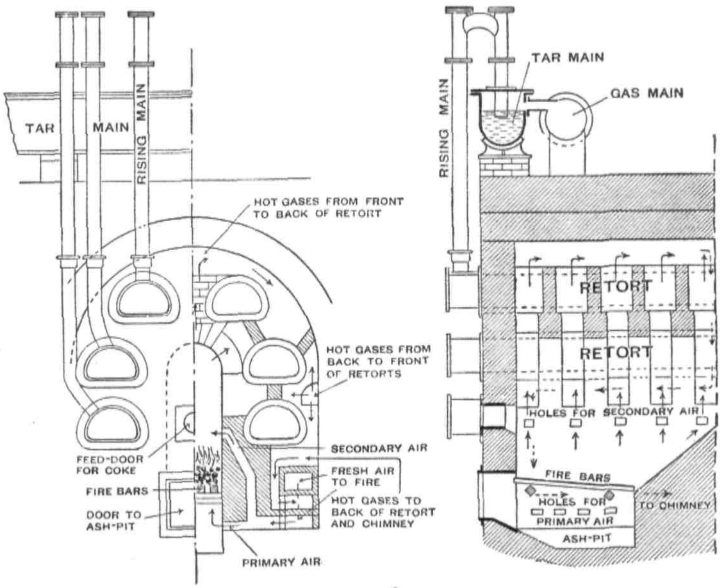


FIG. 178.—COAL-GAS RETORTS WITH GAS-FIRING. (After Butterfield.)

about 20 feet so as to provide a continuous channel right through the furnace, with a door at each end. The hot gases from the retort are taken off by a "rising main" (Fig. 178), and pass through a trap in the "tar-main" into the "gas-main." Air-cooled condensers (Fig. 179) are used to throw down from the gas a further quantity of tar, water, and ammonia. The gas then passes through a rotary air-pump, known as the exhauster, which serves to maintain a slight negative pressure on the retorts. Washers and scrubbers are used to extract the ammonia from the gas by means of water, whilst oxide of iron in the purifiers removes hydrogen sulphide and cyanogen-compounds. The purified gas passes from the purifiers through a meter to the gas-holder for distribution.

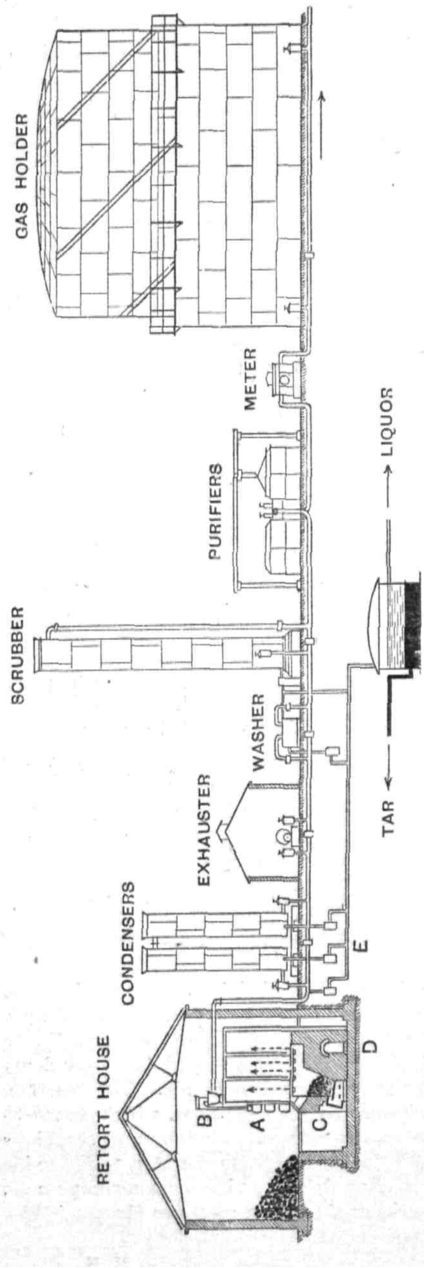


FIG. 179.—PLANT FOR MANUFACTURE OF COAL-GAS. (After Cristopherson.)

The principal impurity in the gas is sulphur, in the form of sulphuretted hydrogen, H_2S, and carbon disulphide, CS_2. By passing the gas over finely-divided nickel, the carbon disulphide can be converted into methane and hydrogen sulphide,

$$CS_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2S;$$

almost the whole of the sulphur can then be removed by absorption in oxide of iron, from which the sulphur is recovered (after extracting cyanogen-compounds, p. 475) by burning to sulphur dioxide, *and converting the sulphur* dioxide into sulphuric acid.

The luminosity of coal gas is due chiefly to ethylene, and to the vapours of benzene, naphthalene, etc.; the benzene and toluene in the gas can be removed and recovered by absorption in "creosote oil," whilst the deposition of solid naphthalene is a frequent source of blockage of gas pipes in cold weather. Coal gas is often diluted with "water gas" (see below), its luminosity being maintained if necessary by the products of decomposition of mineral oil which are present in "carburetted water gas." The luminosity of coal gas may also be increased by bubbling it through volatile hydrocarbons, such as petrol; a gas

suitable for use with incandescent mantles (p. 680), Bunsen burners, etc., can be prepared by saturating air with the vapours of petrol, and is known as PETROL GAS.

(*c*) **Producer gas.** — When a limited supply of air is passed into a fire, the carbon dioxide that is first formed is reduced by the further action of the hot fuel, and carbon monoxide is produced. This may be allowed to burn with a blue flame on the surface of the fuel, or the additional air required to burn it may be admitted at some distance from the fire; thus, in the GAS-FIRING of retorts (Fig. 178), carbon monoxide is produced by admitting a regulated supply of air to the fuel through a small orifice under the fire-bars, and combustion is effected by the introduction of "secondary" air below the retorts. The gas may also be made in a PRODUCER (Fig. 180) and distributed

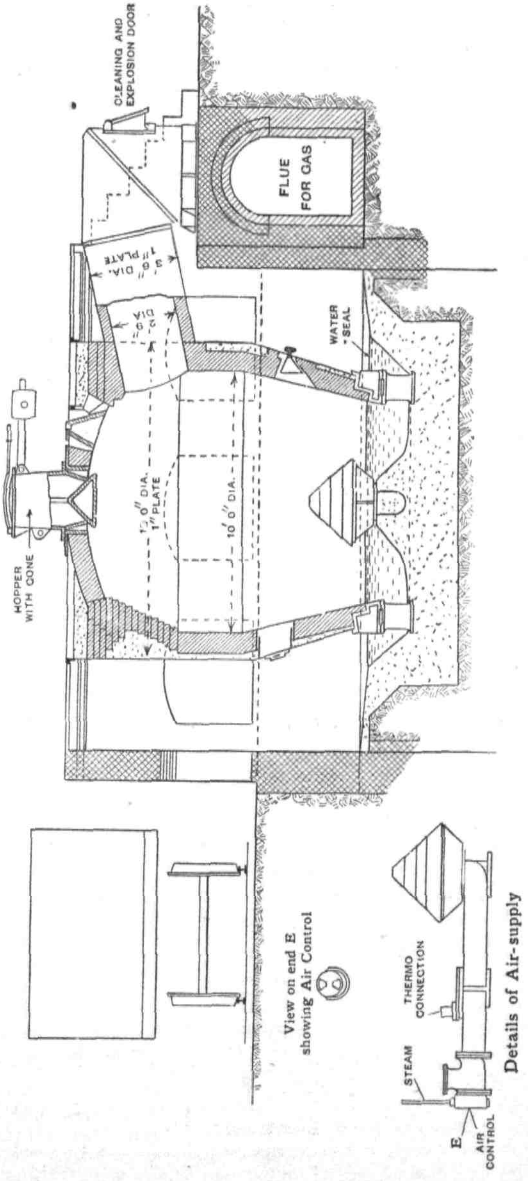


FIG. 180.—GAS PRODUCER.

through pipes as PRODUCER GAS to a series of furnaces or to gas engines.

In Fig. 178 the system of gas-firing includes a scheme of recuperative heating (compare Fig. 191, p. 499) whereby the incoming air is drawn through flues heated by the gases escaping from the furnace. In Fig. 180 a separate producer is shown in which the fuel is admitted through a hopper, provided with a cone which can be opened to drop the fuel into the producer after the cover has been closed, so as to prevent the escape of gas. A regulated supply of air is blown into the bottom of the furnace under a conical baffle with the help of a steam-injector, and the producer gas passes from a pipe in the top of the producer to a flue, which leads the hot gas directly to the furnaces. This system of heating has displaced almost completely the system of gas-firing described above, in the manufacture of coal gas as well as in steel furnaces (Fig. 260, p. 768) and zinc furnaces (Fig. 282, p. 869); the original system of gas-firing is, however, still in use for heating steam boilers, a regenerative effect being introduced by heating the feed-water by the gases passing to the chimney.

Since oxygen yields twice its volume of carbon monoxide, producer gas should be a mixture of nitrogen with about half its volume of carbon monoxide; but unless the producer is worked at the highest possible temperature a considerable proportion of carbon dioxide may also be formed. The presence of water vapour in the air (especially when injected into the producer by means of a steam jet) also gives rise to hydrogen and a small amount of methane. The composition of producer gas may be shown in comparison with blast-furnace gas (p. 764) as follows:

	H_2	CH_4	CO	CO_2	N_2
Producer gas . . .	5	2	29	2	62%
Blast-furnace gas . .	2	1	27	9	61%

In each case there is about 60 per cent. of nitrogen and nearly 30 per cent. of carbon monoxide, but in the producer gas the remaining 10 per cent. is mainly hydrogen and methane, whereas in the blast-furnace gas it is mainly carbon dioxide.

(*d*) **Water Gas.**—The high proportion of nitrogen in producer gas can be avoided by oxidising the carbon to carbon monoxide by means of steam instead of by air. The gas produced in this way is theoretically a mixture of equal volumes of hydrogen and carbon monoxide. WATER GAS actually contains nearly 50 per cent. of hydrogen and is the cheapest source of this gas (see below); but the proportion of carbon monoxide is diminished by about 4 per cent. each of carbon dioxide and of nitrogen, *e.g.*,

	H_2	CH_4	CO	CO_2	N_2
Composition of Water Gas	49	$\frac{1}{2}$	42	4	$4\frac{1}{2}$%

The ordinary form of water-gas burns with a blue flame and is known as BLUE WATER GAS; when luminosity is required, oil is sprayed into the fuel with the steam and CARBURETTED WATER GAS is produced.

The production of water gas is a strongly endothermic action,

$$C + H_2O\ (\text{liq.}) = CO + H_2 - 39{,}360 \text{ calories}$$
$$C + H_2O\ (\text{steam}) = CO + H_2 - 29{,}000 \text{ calories},$$

in marked contrast with the strongly exothermic action used in making producer gas,

$$C + \tfrac{1}{2}O_2 = CO + 29{,}000 \text{ calories};$$

compare also the thermochemical equation,

$$C + O_2 = CO_2 + 96{,}960 \text{ calories},$$

for the complete combustion of carbon. Water gas can therefore only be made intermittently, *e.g.*, for a period of five minutes, during which the temperature of the fuel is falling, alternately with periods of three minutes during which the temperature of the fuel is raised again by blowing in air.

When steam is supplied to the producer at 100° and the gases are led out at 600°, the thermal changes are

$$C\ (\text{solid}) + H_2O\ (\text{steam at } 100°) = CO + H_2\ (600°) - 36{,}450 \text{ calories}$$
$$C\ (\text{solid}) + \tfrac{1}{2}O_2\ (15°) = CO\ (600°) + 17{,}080 \text{ calories}$$
$$C\ (\text{solid}) + O_2\ (15°) = CO_2\ (600°) + 76{,}180 \text{ calories.}$$

It is therefore possible by burning the carbon to carbon dioxide to generate enough heat to convert 76,180/36,450, or roughly twice its weight of carbon, into water gas; whilst when carbon monoxide (in the form of producer gas) is manufactured during the intermediate periods of heating, the carbon converted into water gas is only 17,080/36,450, or rather less than one-half, of that burnt to producer gas.

(*e*) **Semi-Water Gas.**—The best conditions for manufacturing gaseous fuel are obtained by oxidising carbon with a mixture of steam and air in such proportions as to maintain a convenient constant temperature in the producer. Theoretically this condition will be reached when the weights of carbon oxidised by air and by steam are in the ratio, 36,450 : 17,080 = 2·134 : 1, given by the preceding calculation. This corresponds with a vapour pressure of 123 mm. of water vapour in the air supplied to the producer, or a saturation temperature of 56°. The product, which is known as SEMI-WATER GAS, contains approximately 45 per cent. of combustible gases as compared with 36 per cent. when air alone is used, *e.g.*,

	H_2	CH_4	CO	CO_2	N_2
Composition of Semi-Water Gas	14	3	27	4	52%

In this process tar and ammonia can be recovered from bituminous fuel, provided that the output is large enough to justify the plant required for these additional operations. Gas producers have also the advantage that coal containing too high a percentage of ash to be burnt under boilers can be used as a source of gaseous fuel. SUCTION

GAS, prepared from anthracite in a producer through which air and steam are drawn by the suction of a gas engine, provides a very convenient and economical form of power for small plants.

(*f*) **Hydrogen from Water Gas.**—Water gas prepared by the action of steam on hot carbon contains nearly 50 per cent. of hydrogen and more than 40 per cent. of carbonic oxide. The hydrogen was formerly separated by liquefying the other constituents, but a process has now been developed whereby the carbonic oxide in the gas is used to produce a further quantity of hydrogen by reduction of water vapour. This formation of hydrogen is accompanied by a small liberation of heat, since its heat of combustion is slightly less than that of carbon monoxide, and the equilibrium (which is not affected to any marked extent by pressure) is increasingly in favour of the production of hydrogen as the temperature is decreased, *e.g.*, for equimolecular mixtures we have the following data :—

TABLE 54.—THE WATER-GAS EQUILIBRIUM.

	$CO + H_2O$ (steam) $\rightleftharpoons$	$CO_2 + H_2 + 10{,}200$ calories.
At 400° . .	6%	94%
,, 500° . .	14	86
,, 600° . .	24	76
,, 800° . .	47	53
,, 1000° . .	62	38

By passing a mixture of water gas with an excess of steam over a specially active form of iron or copper, a sufficient velocity of change can be reached at temperatures well below 500°, and under these conditions a high ratio of conversion can be realised. It is suggested that oxide of iron acts merely as a "carrier" of oxygen from the water to the carbonic oxide, but that copper acts by decomposing formic acid produced as an intermediate additive product from carbonic oxide and steam.

$$CO + H_2O \rightleftharpoons H{\cdot}CO{\cdot}OH \rightleftharpoons H_2 + CO_2.$$

Liquid Fuels : Petroleum.

The most important of the liquid fuels is mineral oil or PETROLEUM, a complex mixture of hydrocarbons of which accumulations are found in porous rocks, *e.g.*, limestone, protected by some impermeable material. The origin of petroleum is obscure ; it may be of inorganic origin *e.g.*, from carbides, but its optical activity (*i.e.*, its power of rotating the plane of polarisation of light) suggests that it is derived from organic materials, either vegetable or animal (including fishes and molluscs), carried down in sediments and gradually decomposed, perhaps in presence of salts. Petroleum is very widely diffused in sedimentary rocks, although large accumulations are not common.

When a natural deposit of oil is struck, there is usually a large

escape of NATURAL GAS, which may be trapped and utilised. The crude oil which then flows, or is pumped, from the wells, is separated by fractional distillation into PETROL, PARAFFIN OIL, LIGHT LUBRICATING OIL, HEAVY LUBRICATING OIL, MINERAL JELLY, and PARAFFIN WAX, leaving behind a residue of pitch or coke. A natural pitch is found as ASPHALTE or BITUMEN, *e.g.*, in the Pitch Lake of Trinidad, which occupies the crater of an old mud-volcano or geyser; this resembles the residue from the distillation of petroleum, but is modified by the presence of a high proportion (up to 10 per cent.) of sulphur.

(*a*) *American petroleum* consists mainly of PARAFFINS of the series C_nH_{2n+2}, of which methane, CH_4 (or hydrogen, H_2), is the first member. The hydrocarbons from CH_4 to C_4H_{10} are gases, from C_5H_{12} to $C_{13}H_{28}$ they are liquids, whilst the higher members which have been identified up to $C_{35}H_{72}$ are solids, the boiling-points and melting-points rising steadily as the size of the molecule increases.

(*b*) *Russian petroleum* consists largely of homologues of ethylene, C_2H_4, with the general formula C_nH_{2n}. These compounds are mainly chemically-inactive CYCLOPARAFFINS or POLYMETHYLENE COMPOUNDS containing rings of methylene groups $—CH_2—$.

(*c*) *Borneo petroleum* is of special interest as containing a large proportion of aromatic hydrocarbons of the series C_nH_{2n-6}, including

Benzene, C_6H_6
Toluene, C_7H_8, or $C_6H_5{\cdot}CH_3$
Xylene, C_8H_{10}, or $C_6H_4(CH_3)_2$, etc.

(*d*) *Other Liquid Fuels.*—COAL-TAR and its fractions, *e.g.*, a high-boiling CREOSOTE OIL, and mixtures of petroleum with tar and with powdered coal, have been used successfully for steam raising, whilst ALCOHOL and BENZENE are used as alternatives to petrol in internal combustion engines.

Solid Fuels: Wood, Peat, Lignite, and Coal.

The most important fuel, and the principal source of power at the present time, consists of COAL, formed by the gradual elimination of hydrogen and oxygen from decaying vegetation. The successive stages in the formation of coal are seen in—

(*a*) PEAT, the value of which as a fuel is restricted severely by the large proportion of water which it contains and the tenacity with which it holds it.

(*b*) LIGNITE, or soft brown coal, a low grade fuel intermediate between peat and coal.

(*c*) BITUMINOUS COAL, which gives large quantities of volatile matter when heated, and is therefore used in the manufacture of gas and coal-tar, as well as for open fires.

(*d*) ANTHRACITE, a hard coal which burns with very little smoke,

and is of special value as a fuel for steam-raising and for use in enclosed stoves.

The changes of composition which take place during the conversion of vegetable matter into coal are shown in the following table, in which the average composition of a large number of samples of each type of fuel is given on an ash-free basis.

TABLE 55.—PERCENTAGE COMPOSITION OF SOLID FUELS.

	C.	H.	N.	O.
Wood	50	6	1	43
Peat	55	6	2	37
Lignite	73	5	1	21
Bituminous coal . .	85	5	1	9
Anthracite . . .	93	3	1	3

The progressive elimination of oxygen and hydrogen is seen more clearly by tabulating the composition relatively to 100 parts of carbon.

TABLE 56.—COMPOSITION OF SOLID FUELS.

	C.	H.	N.	O.
Wood	100	$12\frac{1}{2}$	2	87
Peat	100	11	4	67
Lignite	100	7	2	28
Bituminous coal . .	100	7	2	10
Anthracite . . .	100	3	1	3

The hydrogen and oxygen are present initially in almost the same proportions as in water, but the oxygen is eliminated much more rapidly than the hydrogen, with the result that anthracite contains approximately equal weights of these two elements. There is also a very slow elimination of nitrogen. Peat contains an abnormally high proportion of nitrogen; this is perhaps due to a fixation of nitrogen from the air by bacteria, since the mosses from which peat is derived do not contain this excessive proportion of nitrogen.

Calorific Value of Fuels.

The value of a fuel is measured by its CALORIFIC POWER, *i.e.*, the calories of heat produced by burning 1 gram.

(*a*) The calorific value of a *solid fuel* is usually less than that of the carbon and hydrogen which it contains, on account of the heat evolved in the combination of these elements with the oxygen of the fuel. Thus the heat of combustion of 1 gram of carbon is 96,960/12 or about 8000 calories, and that of hydrogen is 68,360/2 or about 34,000 calories, but the calorific value of a solid fuel is usually below 8000 calories and increases as hydrogen is eliminated; *e.g.*, wood has a calorific value of about 4000 calories, whilst the calorific value of anthracite is practically equal to the value for pure carbon, namely, 8000 calories.

The calorific value of coal is also influenced very greatly by the proportion of incombustible ash which it contains. This may be reduced by picking over the coal to remove shale, slate, etc., or by "washing" it, when the denser shale sinks to the bottom and can be removed, whilst the dust (which always contains an excessive proportion of ash) is separated from the harder and purer coal.

(*b*) The calorific value of a *liquid fuel* is usually higher than that of coal, *e.g.*, 1 gram of petroleum usually gives rather more than 10,000 calories, the low-boiling petrols give about 11,000 calories, and pure benzene gives just under 10,000 calories; industrial alcohol, on the other hand, gives only about 6000 calories per gram.

(*c*) The calorific value of a *gaseous fuel* measured in British thermal units * (*i.e.*, pounds of water raised 1° F.) per cubic foot of gas is approximately as follows:

Blast-furnace gas	100	B.Th.U.
Air-producer or suction-gas . . .	130	,,
Semi-water gas	150	,,
Blue water gas	300	,,
Coal gas, coke-oven gas or carburetted water gas.	500	,,
Natural gas	1000	,,

Carbon and Sulphur.

Carbon disulphide, CS_2, is prepared by the direct combination of carbon with sulphur in an electric furnace (Fig. 181).

In this process for the manufacture of carbon disulphide heat is supplied by electric currents passing between four electrodes *AA*, each containing 25 blocks of carbon 4 × 4 × 48 inches, and separated by about 12 inches from one another in the centre of the furnace. The space between these is bridged by broken carbons fed in at *BB*. The shaft of the furnace is filled with charcoal *C*. The space *D* below the electrodes is filled with liquid sulphur, and sulphur fed in at *E* and *F* is also used to jacket the furnace, so that almost the whole of the heat escaping through the walls is caught and carried back either by the charcoal or by the sulphur passing down to the electrodes. The furnace is about 8 feet in diameter at the base and about 20 feet in height over all (hearth = 6 feet, shaft = 8 feet, head = 4 feet). It has a capacity of about 10 tons of carbon bisulphide per day of 24 hours.

Carbon disulphide is a volatile liquid, of density 1·3 at 0°, boiling at 46° and freezing at − 110°. It is a poisonous substance which is used as an insecticide and for killing vermin. It is a good solvent for many substances, including sulphur, phosphorus, rubber, and many organic compounds such as fats; but on account of its extreme inflammability it has been largely displaced by the chlorine compounds described above. The heavy vapour forms a highly explosive mixture with air. When pure, it has a fragrant odour, but it is usually contaminated with malodorous sulphur compounds; these may be

* 1 Therm = 100,000 B.Th.U.

removed by contact with mercury, or by the prolonged action of concentrated sulphuric acid, followed by distillation.

Carbon disulphide is an endothermic compound; its heat of formation can be deduced from heats of combustion of carbon, sulphur, and carbon disulphide, as follows:

Combustion of carbon

$$C \text{ (charcoal)} + O_2 = CO_2 \quad + 96,960 \text{ cal.}$$

Combustion of sulphur

$$S_2 \text{ (rhombic)} + 2O_2 = 2SO_2 \quad + 142,060 \text{ cal.}$$

Combustion of carbon disulphide

$$CS_2 \text{ (vapour)} + 3O_2 = CO_2 + 2SO_2 + 265,030 \text{ cal.}$$

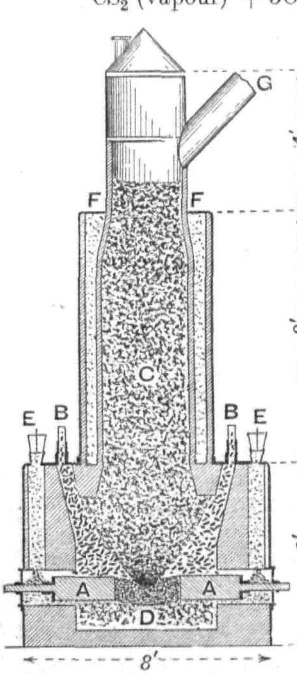


FIG. 181.—ELECTRIC FURNACE FOR CARBON DISULPHIDE. (E. R. Taylor.)

The heat of combustion of the elements is $96,960 + 142,060 = 239,020$, whilst the heat of combustion of the compound is 265,030 calories. The heat of formation of the compound is therefore $239,020 - 265,030 = -26,010$ calories, or

$$C \text{ (charcoal)} + S_2 \text{ (rhombic)} = CS_2 \text{ (vapour)} - 26,010 \text{ cal.}$$

Carbon monosulphide, CS, the analogue of carbon monoxide, is prepared by passing a rapid stream of carbon disulphide vapour through an ozoniser. The products of the action are cooled with liquid air, when the monosulphide is deposited as a liquid along with the unchanged carbon disulphide. When the temperature of the liquid is allowed to rise, the monosulphide polymerises with explosive violence to form a brown solid, $(CS)_x$.

Carbon oxysulphide, COS, may be prepared by the action of sulphuric anhydride on carbon disulphide,

$$CS_2 + 3SO_3 = COS + 4SO_2,$$

$$\text{compare} \quad CCl_4 + 2SO_3 = COCl_2 + S_2O_5Cl_2,$$

or by the action of sulphuric acid on potassium sulphocyanide, KCNS,

$$2KSCN + 2H_2SO_4 + 2H_2O = K_2SO_4 + (NH_4)_2SO_4 + 2COS.$$

It is a colourless, odourless gas which dissolves in its own volume of water and burns with a blue flame,

$$2COS + 3O_2 = 2CO_2 + 2SO_2.$$

CARBON AND NITROGEN.

Nitrogenous Compounds of Carbon.

(*a*) *Proteins.*—The nitrogenous organic compounds, such as ALBUMEN and PROTEIN, which play so important a part in vital chemistry, are derivatives of **aminoacetic acid**, $NH_2 \cdot CH_2 \cdot CO \cdot OH$. Long chains, in which the group —NH·CHX·CO— is the unit, are formed by eliminating water from AMINO-ACIDS of the type $NH_2 \cdot CHX \cdot CO \cdot OH$. These chain compounds are broken down into simple amino-acids during digestion and built up again in the tissues during assimilation.

(*b*) *Nitro-compounds and Nitrates.*—Nitrogen is also present in organic NITRO-COMPOUNDS such as **picric acid**, $C_6H_2(NO_2)_3 \cdot OH$, prepared by the action of nitric acid on "carbolic acid" or **phenol**, $C_6H_5 \cdot OH$, and **trinitrotoluene**, $C_6H_2(NO_2)_3 \cdot CH_3$, prepared by the action of nitric acid on **toluene**, $C_6H_5 \cdot CH_3$. The organic NITRATES such as GUN-COTTON or **nitro-cellulose**, prepared by the action of nitric acid on cotton, and **nitro-glycerine**, $C_3H_5(NO_3)_3$, prepared by the action of nitric acid on **glycerine**, $C_3H_5(OH)_3$, are nitrates of the more complex alcohols, *e.g.*,

$$\underset{\text{Glycerine}}{C_3H_5(OH)_3} + 3HNO_3 = \underset{\text{Nitroglycerine}}{C_3H_5(NO_3)_3} + 3H_2O$$

compare $Al(OH)_3 + 3HNO_3 = Al(NO_3)_3 + 3H_2O$.

In all these compounds the nitrogen serves the same purpose as in the nitrate radical of ammonium nitrate, $NH_4 \cdot NO_3$, in bringing oxygen into the molecule of a combustible compound and so producing a powerful explosive. The water produced in "nitration" is absorbed by nitrating in presence of sulphuric acid.

(*c*) *Cyanides.*—The most stable compounds of carbon and nitrogen are those which contain the univalent cyanogen radical, —CN (see below).

Cyanogen Compounds.

(*a*) *The Cyanogen Radical.*—In the cyanogen compounds the univalent radical **cyanogen**, —CN, usually behaves like an atom of one of the halogen elements. **Cyanogen**, CN, and **ammonium**, NH_4, were indeed two of the earliest examples of a COMPOUND RADICAL, *i.e.*, a group of atoms taking the place and playing the part of a single atom, in the one case of a non-metal such as chlorine, and, in the other case, of a metal such as potassium or sodium. This analogy is sometimes expressed by writing cyanogen as Cy, compare Cl, and ammonium as Am, compare K or Na.

(*b*) *Hydrocyanic Acid and the Cyanides.*—As this analogy to the halogens would suggest, the most important cyanogen compounds are those in which the radical is combined with hydrogen to form **hydrocyanic acid**, HCN, or with metals to form CYANIDES such as **potassium**

cyanide, KCN (p. 479), as well as DOUBLE CYANIDES such as **potassium ferrocyanide**, $K_4FeC_6N_6$ (pp. 480 and 787). The free radical, **dicyanogen**, C_2N_2, or cyanogen gas, is known (p. 477), but is of no technical importance.

(*c*) *Comparison with the Halogens.*—Whilst cyanogen shows a broad general resemblance to chlorine, the following points of contrast may be noticed :

(i) Hydrocyanic acid, HCN, is a very weak acid with a very small affinity for water ; it can therefore be displaced from its salts even by atmospheric carbon dioxide.

(ii) On the other hand, it has a far greater tendency than hydrochloric acid to form stable double salts. Thus, although double chlorides, such as $NaAuCl_4$ and K_2PtCl_6, are well known, these compounds are as a rule decomposed readily, so that the metals in the negative radical can easily be detected and separated. On the other hand, the FERROCYANIDES, such as **potassium ferrocyanide**, $K_4FeC_6N_6$, and the FERRICYANIDES, such as **potassium ferricyanide**, $K_3FeC_6N_6$, are so stable that the iron in the negative radical is completely disguised and cannot be detected by the ordinary reagents for ferrous or ferric salts.

(iii) Cyanogen differs from chlorine, just as ammonium differs from sodium and potassium, in that the compound radical may break down and give rise to products for which no analogy exists in the case of the simple radicals. Thus, a number of reactions are known in which the nitrogen of the cyanogen compounds is eliminated in the form of ammonia, *e.g.*,

$$K_4FeC_6N_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO \text{ and } CaCN_2 + 3H_2O = CaCO_3 + 2NH_3.$$

(*d*) *Thermochemistry.*—The cyanogen radical is strongly endothermic, so that as a rule cyanides are only produced when metals are present so as to give rise to metallic cyanides, or the still more stable double cyanides. Typical data are as follows :—

TABLE 57.—HEATS OF FORMATION OF CYANOGEN COMPOUNDS.

Dicyanogen	C_2N_2	− 66,000 calories
Hydrocyanic acid . . .	HCN	− 27,000 ,,
	HCN aq.	− 22,000 ,,
Potassium cyanide . . .	KCN	+ 32,000 ,,
Potassium sulphocyanide . .	KCNS	+ 50,000 ,,
Potassium cyanate . . .	KCNO	+ 102,000 ,,
Potassium ferrocyanide . .	$K_4FeC_6N_6$	+ 137,000 ,,

Preparation of Cyanogen Compounds.

(*a*) *From Organic Nitrogen Compounds.*—When an organic compound containing nitrogen is heated with metallic sodium, **sodium cyanide**, NaCN, is produced and can be used as a qualitative test for the presence

of nitrogen. In much the same way, **potassium cyanide**, KCN, was formerly prepared by heating nitrogenous organic matter (horns, hoofs, hides) with potassium carbonate and metallic iron ; this preparation probably depends on the interaction of carbon and ammonia (see below),

$$NH_3 + C = HCN + H_2 \quad \text{or}$$
$$K_2CO_3 + 2NH_3 + 4C = 2KCN + 3H_2 + 3CO.$$

The product was isolated in the form of potassium ferrocyanide, $K_4FeC_6N_6$, on account of the readiness with which this salt separates in crystalline form, and was reconverted into the cyanide (i) by ignition, when one-third of the nitrogen was lost,

$$K_4FeC_6N_6 = 4KCN + Fe + 2C + N_2,$$

or (ii) by the action of metallic sodium, when the whole of the cyanogen was recovered as a mixture of sodium and potassium cyanides, containing a higher proportion of cyanogen than pure potassium cyanide,

$$K_4FeC_6N_6 + 2Na = 4KCN + 2NaCN + Fe.$$

(*b*) *Bucher Process.*—In the Bucher process for fixing nitrogen, a mixture of sodium carbonate and carbon, with iron as a catalyst, is made into porous bricks and heated in an atmosphere of nitrogen. **Sodium cyanide**, NaCN, is produced and can be extracted most effectively by means of anhydrous liquid ammonia, leaving the bricks in a condition suitable for reworking,

$$Na_2CO_3 + 4C + N_2 = 2NaCN + 3CO.$$

(*c*) *From Carbides.*—When calcium carbide absorbs nitrogen it gives a mixture of carbon and **calcium cyanamide**, $CaCN_2$ (p. 626), from which **sodium cyanide** can be prepared by fusion with sodium carbonate,

$$CaCN_2 + C + Na_2CO_3 = CaCO_3 + 2NaCN.$$

Under similar conditions, barium carbide is converted directly into **barium cyanide**,

$$BaC_2 + N_2 = BaC_2N_2.$$

Cyanogen and Paracyanogen.

Cyanogen-gas or **dicyanogen,** C_2N_2, may be prepared in a free state by heating to a red heat the cyanide of mercury, silver, or gold :

$$\begin{aligned} HgC_2N_2 &= Hg + C_2N_2 \\ 2AgCN &= 2Ag + C_2N_2 \\ 2AuC_3N_3 &= 2Au + 3C_2N_2 \\ \text{compare } 2AuCl_3 &= 2Au + 3Cl_2. \end{aligned}$$

It is a colourless, poisonous gas, with a characteristic smell, and burns with a purple flame. It condenses to a colourless liquid which boils at $-21°$ and freezes at $-34°$.

Water at 0° dissolves four times its own volume of the gas. On exposure to light, the solution gives ammonium oxalate, $(CO{\cdot}ONH_4)_2$, ammonium formate, $H{\cdot}CO{\cdot}ONH_4$, hydrogen cyanide, HCN, and urea, $CO(NH_2)_2$. The formation of these products probably depends on the following actions :

(i) $C_2N_2 + 4H_2O = \underset{\text{Ammonium oxalate}}{(CO{\cdot}ONH_4)_2}$

(ii) $C_2N_2 + H_2O = \underset{\text{Hydrocyanic acid}}{HCN} + \underset{\text{Cyanic acid}}{HCNO}$

compare $Cl_2 + H_2O = HCl + HClO$

(iii) $HCN + 2H_2O = \underset{\text{Ammonium formate}}{H{\cdot}CO{\cdot}ONH_4}$

(iv) $HCNO + NH_3 = \underset{\text{Urea}}{CO(NH_2)_2}$

Paracyanogen, $(CN)_n$, a polymer of cyanogen, is left as a brown powder when mercury cyanide is heated to 450°. It is insoluble in water and is converted by heat into cyanogen.

Hydrogen Cyanide, Hydrocyanic Acid, or Prussic Acid, HCN.

(*a*) *Preparation.* (i) Hydrogen cyanide may be synthesised by passing ammonia over charcoal heated to 1000°,

$$\underset{+\,12{,}000}{NH_3} + C \rightleftharpoons \underset{-\,27{,}000}{HCN} + H_2 - 39{,}000 \text{ calories.}$$

The action is strongly endothermic and gives an increasing proportion of hydrogen cyanide as the temperature is raised, *e.g.*, the ratio of the concentrations,

$$\frac{C_{NH_3}}{C_{HCN} \times C_{H_2}} = 632 \text{ at } 500°, \text{ but}$$
$$= 0{\cdot}003 \text{ at } 1100°.$$

(ii) An aqueous solution of hydrogen cyanide may be prepared by *distilling a cyanide with dilute sulphuric acid*,

$$KCN + H_2SO_4 = KHSO_4 + HCN.$$

(iii) Anhydrous hydrogen cyanide may be prepared by heating a powdered mixture of potassium cyanide and potassium hydrogen sulphide,

$$KCN + KSH = K_2S + HCN.$$

(*b*) *General Properties.*—Hydrogen cyanide condenses as a colourless liquid which boils at 26° and freezes at − 15°. It has a characteristic odour and is extremely poisonous ; the best antidote is freshly precipitated ferrous hydroxide (*e.g.*, a mixture of ferrous sulphate and sodium carbonate) accompanied by the stimulating action of ammonia. The vapour burns with a beautiful peach-blossom coloured flame,

$$4HCN + 5O_2 = 4CO_2 + 2H_2O + 2N_2.$$

(*c*) *Acid Properties.*—Hydrogen cyanide is freely soluble in water and imparts to it an acid reaction. It forms a series of CYANIDES, but

is an extremely weak acid, as is shown by the fact that the soluble cyanides are appreciably hydrolysed by water; thus, a solution of potassium cyanide has an alkaline reaction and smells of hydrogen cyanide (compare p. 205),

$$KCN + H_2O \rightleftharpoons HCN + KOH.$$

When a metallic cyanide is acted on by a dilute acid, hydrogen cyanide is liberated,

$$KCN + H_2SO_4 = KHSO_4 + HCN;$$

but if concentrated sulphuric acid be used, the cyanide is decomposed completely and carbon monoxide is set free,

$$2KCN + 2H_2SO_4 + 2H_2O = K_2SO_4 + (NH_4)_2SO_4 + 2CO.$$

In this action formic acid, which gives carbon monoxide when acted on by sulphuric acid (p. 460), is perhaps an intermediate product,

$$HCN + 2H_2O = H{\cdot}CO{\cdot}ONH_4 \text{ (ammonium formate)}$$
$$H{\cdot}CO{\cdot}OH = CO + H_2O.$$

(*c*) *Constitution.*—(i) *Hydrocyanic acid* may be either

Hydrogen cyanide, $H{-}C{\equiv}N$, or
Hydrogen isocyanide, $H{-}N{=}C{<}$,

since organic derivatives corresponding with both formulæ are known, *e.g.*, ethyl cyanide, $C_2H_5{\cdot}C{\equiv}N$, ethyl isocyanide, $C_2H_5{\cdot}N{=}C{<}$. Liquid hydrocyanic acid is perhaps a mixture of the two isomeric compounds,

$$H{\cdot}C{\equiv}N \rightleftharpoons H{\cdot}N{=}C{<}.$$

(ii) The *metallic cyanides* may be derived from either formula, but as potassium cyanide gives normal organic cyanides where silver cyanide gives isocyanides, it is possible that they should be represented thus:

Potassium cyanide, $K{\cdot}C{\equiv}N$. Silver *iso*cyanide, $Ag{\cdot}N{=}C{<}$.

(iii) *Cyanogen* is undoubtedly $\begin{array}{c}C{\equiv}N\\ |\\ C{\equiv}N\end{array}$, since it can be hydrolysed to ammonium oxalate, which has the constitution $\begin{array}{c}CO{\cdot}ONH_4\\ |\\ CO{\cdot}ONH_4\end{array}$.

Metallic Cyanides.

The general methods of preparation of the cyanides have already been described. The following points may be noted in reference to their properties.

Potassium cyanide, KCN, is a soluble salt with an alkaline reaction. It melts at a red heat and on cooling crystallises in anhydrous cubes; it may also be volatilised at a high temperature without decomposition. It is used in electroplating and for the extraction of gold from its ores,

$$8KCN + 4Au + O_2 + 2H_2O = 4KAuC_2N_2 + 4KOH.$$

Mercuric cyanide, HgC_2N_2, prepared by dissolving mercuric oxide in a boiling solution of hydrogen cyanide,

$$HgO + 2HCN = HgC_2N_2 + H_2O,$$

separates from water in colourless anhydrous crystals. It is soluble in water, but the solution is not an electrolyte and hydrocyanic acid is only set free when the compound is boiled with a strong acid.

Silver cyanide, $AgCN$, is formed as a white precipitate by adding a solution of silver nitrate to a solution of potassium cyanide,

$$KCN + AgNO_3 = AgCN + KNO_3.$$

It is insoluble in cold dilute nitric acid, but dissolves readily in ammonia and in a solution of potassium cyanide. The soluble double cyanide, **potassium argenticyanide,** $KAgC_2N_2$, prepared by dissolving silver nitrate in an excess of potassium cyanide, is largely used in electroplating (p. 849).

Potassium ferrocyanide, or "yellow prussiate of potash," $K_4FeC_6N_6$ (p. 787), which contains iron in a ferrous condition ($4KCN + FeC_2N_2$), may be prepared by mixing solutions of potassium cyanide and ferrous sulphate,

$$6KCN + FeSO_4 = K_4FeC_6N_6 + K_2SO_4,$$

as well as by the commercial method described above. It separates from water in yellow, tetragonal crystals of the composition $K_4FeC_6N_6,3H_2O$, and is oxidised by chlorine to **potassium ferricyanide** or "red prussiate of potash" (p. 790), $K_3FeC_6N_6$, in which the iron is in the ferric condition ($3KCN + FeC_3N_3$),

$$2K_4FeC_6N_6 + Cl_2 = 2K_3FeC_6N_6 + 2KCl.$$

Cyanic Acid and the Cyanates.

Potassium cyanide acts as a powerful reducing agent, *e.g.*, in metallurgy, not only because of the unburnt carbon which it contains, but also because the compound is able to unite as a whole with oxygen to form **potassium cyanate**, $KCNO$, *e.g.*,

$$KCN + PbO = KCNO + Pb,$$

a compound which crystallises from water in shining leaflets.

Ammonium cyanate, $NH_4{\cdot}CNO$, is of interest because it is ISOMERIC with **carbamide** or **urea,** $CO(NH_2)_2$, since both compounds have the same molecular formula, CON_2H_4. It can be prepared by mixing the vapour of cyanic acid with dry ammonia, but in solution is largely converted into urea by a reversible process of ISOMERIC CHANGE,

$$NH_4{\cdot}CNO \rightleftharpoons CO(NH_2)_2.$$

When the aqueous solution is evaporated to dryness, urea crystallises out and the isomeric change passes to completion; urea is therefore

produced instead of ammonium cyanate when an aqueous solution of potassium cyanate and ammonium sulphate is evaporated.

$$2KCNO+(NH_4)_2SO_4 \rightleftharpoons K_2SO_4+2NH_4\cdot CNO=K_2SO_4+2CO(NH_2)_2.$$

Cyanic acid, $HO\cdot CN$, can be prepared by distilling urea,

$$CO(NH_2)_2 \rightleftharpoons HCNO + NH_3.$$

It is a volatile liquid with a strong acid reaction and smells like acetic acid. It may be represented either as $HO\cdot C\equiv N$ or as $HN=C=O$.

Thiocyanic Acid and the Thiocyanates.

Potassium thiocyanate or **potassium sulphocyanide,*** KCNS, may be prepared by heating potassium cyanide with sulphur,

$$KCN + S = KCNS.$$

It crystallises in anhydrous prisms, which melt at 174°. It is very deliquescent and readily soluble in water. It gives a white precipitate of **silver thiocyanate, AgCNS**, with aqueous solutions of silver salts, and may be used to estimate silver by titration. With ferric chloride, it gives a soluble blood-red **ferric thiocyanate**, $Fe(CNS)_3$,

$$FeCl_3 + 3KCNS \rightleftharpoons Fe(CNS)_3 + 3KCl,$$

which is used as a qualitative test for ferric salts and for thiocyanates. **Ammonium thiocyanate,** $NH_4\cdot CNS$, resembles the potassium salt.

Thiocyanic acid, HCNS, prepared by distilling potassium thiocyanate with dilute sulphuric acid, is a liquid with a powerful odour ; but when removed from a cooling mixture it polymerises with evolution of heat to a yellow, amorphous body.

* *i.e.*, Potassium cyanate with sulphur *replacing* oxygen, or potassium cyanide with the *addition* of sulphur. It is unfortunate that only one analogous term is available for both uses in the case of selenium.

CHAPTER XXIX

SILICON AND BORON

A. Silicon. Si = 28·3.

Carbon, Silicon, and Boron.

The three elements, carbon, silicon, and boron, may be compared with the three elements, nitrogen, phosphorus, and sulphur. Thus, *carbon* and *silicon* are usually grouped together (just as nitrogen and phosphorus are) because their valencies are the same and therefore the formulæ of their compounds are similar; the two elements and their compounds are, however, widely different both in their chemical and in their physical properties, *e.g.*, it would be difficult to recognise any real similarity between carbonic anhydride, CO_2, and silica, SiO_2, except in the chemical formulæ assigned to them. On the other hand, *silicon* and *boron* show the same broad general similarity as phosphorus and sulphur, both as elements and in their compounds; owing, however, to their different valencies they are generally considered separately and the points of resemblance between them are liable to be overlooked.

Occurrence of Silicon.

Silicon holds the same prominent position in mineral chemistry that is occupied by carbon in vegetable and animal chemistry. Whereas, however, carbon forms very few oxides and a vast number of hydrides, the hydrides of silicon are only of theoretical interest, and it is the oxide, SiO_2, which dominates mineral chemistry. After allowing for the oxygen with which it is combined, the proportion of silicon in the crust of the earth (including the oceans and the atmosphere, which do not contain silica) is about 26 per cent. as compared with 50 per cent. of oxygen, this being the only element which is more abundant than silicon.

(*a*) *Free Silica* is found in a microcrystalline or "cryptocrystalline" form (Greek, κρυπτός, hidden) as FLINT and as AGATE (Fig. 182); flints are found in vast numbers as nodules in deposits of chalk, and provided materials for the earliest tools and weapons. Crystalline silica, in the form of QUARTZ, on the other hand, is found in considerable quantities in MINERAL VEINS, and in still larger quantities in igneous rocks and in the sands and sandstones derived from them.

These mineral veins have their origin in FAULTS, or cracks, in the harder rocks, which were subsequently filled up by minerals. The cracks were formed by disturbances of the type which give rise to earthquakes, but in the softer rocks they are filled up with debris ; and even in the harder rocks large quantities of "country rock" are usually found wherever a mineral vein changes its direction or provides a suitable place for the lodgment of fragments. It is generally assumed that the minerals were deposited from solutions escaping from conditions of high temperature and pressure which cannot easily be reproduced in the laboratory. The veins may include METALLIC ORES such as TINSTONE or CASSITERITE, SnO_2, COPPER PYRITES, $CuFeS_2$, ZINC BLENDE, ZnS, and GALENA, PbS, which usually appear in this order, *e.g.*, tin below copper and zinc below lead, as if this were the order in which they had separated from solution. The upper portions of the vein, or portions remote from the main "spout" through which the minerals entered the vein, are usually occupied by minerals, such as QUARTZ, SiO_2, CALCITE, $CaCO_3$, FLUORSPAR, CaF_2, or BARYTES, $BaSO_4$, and the metallic ores are usually embedded in one or other of these minerals, of which quartz is by far the commonest. Veins of quartz are, indeed, distributed very widely, varying from a fraction of an inch up to 50 ft. or more in thickness. The mining of tin, copper, zinc, and lead depends on discovering these veins, which are usually vertical or only slightly inclined, and following them up through all the complexities of the original fracture. Coal, salt, and the majority of the iron ores, on the other hand, are sedimentary deposits which have been laid down in horizontal seams; these are still more or less flat, but may be intersected by mineral veins or faults which are approximately vertical.

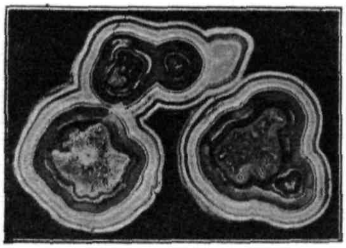


FIG. 182.—AGATE.
(British Museum, Natural History.)

(*b*) *Igneous Rocks.*—The solid crust of the earth consists almost entirely of oxides, including about 60 per cent. of silica and 40 per cent. of bases, the proportions being approximately as follows :

Silica	SiO_2	about	60	per cent.
Alumina	Al_2O_3	,,	15	,,
Magnesia and Lime	MgO and CaO	,,	9	,,
Oxides of Iron	Fe_2O_3 and FeO	,,	6	,,
Soda and Potash	Na_2O and K_2O	,,	6	,,
Water		,,	2	,,
Other acids (TiO_2 0·8, CO_2 0·5, P_2O_5 0·3 per cent., etc.)		,,	1·8	,,
Other bases (BaO 0·1, MnO 0·1 per cent., etc.)		,,	0·3	,,

Apart from alumina, the six principal bases are almost equally abundant; there is, however, rather more lime than magnesia and rather more

soda than potash. Apart from water, all other constituents are present only *in quite small proportions*.

These oxides, originally forming a molten magma, have solidified in IGNEOUS ROCKS as minerals, which are usually compounds rich in silica, although other acid radicals appear occasionally. SEDIMENTARY ROCKS, which are sometimes almost free from silica, are formed from igneous rocks by the solvent and disintegrating action of air and water, followed by precipitation and deposition as sediments under water. Igneous rocks are sometimes found also as intrusions in sedimentary

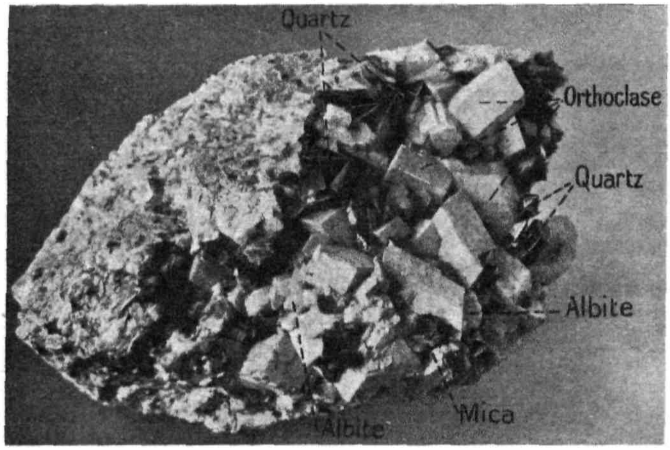


FIG. 183.—GRANITE. (British Museum, Natural History.)
Showing on the left hand the normal crystallisation and cleavage of the mass and on the right hand larger crystals of smoky quartz (black) and orthoclase (grey), with smaller crystals of albite (white) and mica (black) which have grown into a cavity. (About $\frac{2}{3}$ full size.)

rocks, which may be modified profoundly by the high temperatures thereby produced; and lavas may break through the sedimentary rocks and form igneous deposits above them.

The crystallisation of the liquid magma usually gives large crystals when the cooling is slow and small crystals when it is more rapid; in some cases, amorphous or glassy material may also be formed. Thus, GRANITE is a coarsely-crystalline rock composed of three well-defined crystalline MINERALS (Fig. 183):

(i) QUARTZ, composed of pure silica, SiO_2,
(ii) FELSPAR, *e.g.*, ORTHOCLASE, $KAlSi_3O_8$, or ALBITE, $NaAlSi_3O_8$.
(iii) MICA, *e.g.*, BIOTITE, $KHMg_2Al_2(SiO_4)_3$.

RHYOLITE has the same composition as granite, but is an eruptive rock which has solidified more rapidly after being brought to the surface

and released from pressure; it is more minutely crystalline than granite and may contain some uncrystallised glass. OBSIDIAN (Fig. 184) is the same material wholly in the glassy state.

(*c*) *Mineral Silicates.*—The actual minerals are usually more complex than these formulæ would indicate, on account of the formation, by the VICARIOUS REPLACEMENT of one element by another, of isomorphous mixtures to which no simple chemical formula can be given. Thus, whilst silica, SiO_2, is the only acid oxide present in large quantities in the earth's crust and replacement by titanium dioxide, TiO_2, is

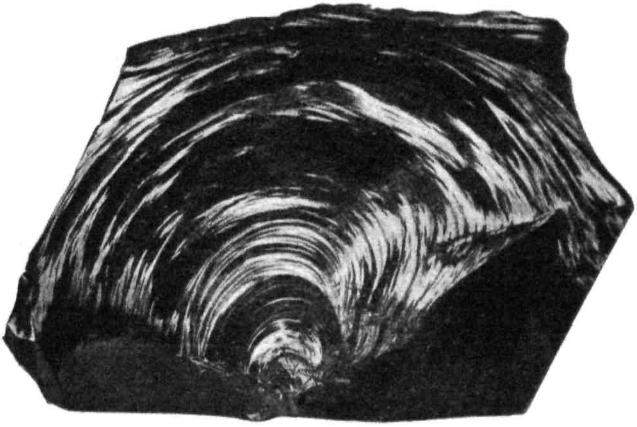


FIG. 184.—OBSIDIAN. (British Museum, Natural History.)
Similar in composition to granite (Fig 183). (About ¾ full size.)

comparatively unimportant, the bases may be divided into three isomorphous groups:

(i) The *alkalies*, Na_2O and K_2O.

(ii) The *alkaline earths* and ferrous oxide, MgO,CaO,FeO.

(iii) The *earth* alumina, and ferric oxide, Al_2O_3 and Fe_2O_3.

Sodium silicates may therefore also contain potassium; calcium silicates may contain magnesium and ferrous iron; and aluminium silicates may contain ferric iron in variable proportions. Thus, in granite, the *quartz* is usually pure silica; but the formula for *felspar* should be shown as

$$[Na,K]AlSi_3O_8,$$

in order to indicate the presence of one atomic proportion of sodium or potassium, or of a mixture of both metals; and the formula of the *mica* may be written

$$[K,Na,Li]H[Mg,Fe'',Ca,Mn]_2[Al,Fe''']_2(SiO_4)_3,$$

in order to include the various elements which it may contain. The square brackets in these formulæ indicate that the number of atomic

proportions shown outside the brackets may be made up in any proportions by the various elements inside the bracket.

The conditions of crystallisation of these minerals are essentially the same as those of salts separating from aqueous solutions or of alloys separating from a melt; but the products are difficult to reproduce in the laboratory, on account of the extreme slowness of crystallisation of the highly viscous magmas, which exhibit a very strong tendency to solidify in a glassy form, even at temperatures above 1000°, when cooled under laboratory conditions, *e.g.*, in the course of a few hours instead of many years. It is also almost impossible to reproduce in the laboratory the extremely high pressures under which crystallisation of rocks may sometimes take place, *e.g.*, at a depth of some miles below the surface of the earth.

Preparation and Properties of Silicon.

(*a*) *Amorphous Silicon.*—Silicon can be prepared

(i) By the action of potassium on potassium silicifluoride (Berzelius, 1823),

$$4K + K_2SiF_6 = Si + 6KF,$$

or by electrolysis of a fused mixture of potassium fluoride and silicifluoride.

(ii) By the action of potassium, sodium, or aluminium on the vapour of silicon tetrachloride,

$$4Na + SiCl_4 = Si + 4NaCl.$$

(iii) By reducing the oxide with magnesium or aluminium,

$$2Mg + SiO_2 = Si + 2MgO.$$

(*b*) *Metallic Silicon.*—The product of these actions is a brown AMORPHOUS SILICON of density of about 2·35. By crystallising it from a metal, *e.g.*, from aluminium (with cryolite as a flux) or from silver, it can be separated in the form of crystals of METALLIC SILICON of density of about 2·5. Metallic silicon is also produced (Fig. 185) when silica is reduced by means of carbon in the electric furnace,

FIG. 185.—METALLIC SILICON. (Full size.)

$$SiO_2 + 2C = Si + 2CO.$$

(*c*) *Properties of Silicon.* — Silicon, although usually classified with the non-metals, on account of the acidic properties of its oxide, etc., is undoubtedly metallic in its general character. Thus, when obtained in a crystalline form it has a steely *metallic lustre*; it also possesses marked *metallic conductivity*, its electrical resistance being a little greater than that of arsenic or antimony, but less than that of bismuth. It also dissolves freely in metals; from some of these, *e.g.*, aluminium

and silver, it crystallises out unchanged, giving rise to well-defined eutectics and V-shaped freezing-point curves ; with others it combines to form SILICIDES (as indicated in Fig. 186), *e.g.*,

Mg_2Si	—	$CaSi_2$	
Mn_2Si	$MnSi$	—	
Fe_2Si	$FeSi$	—	
Co_2Si	$CoSi$	$CoSi_2$	$CoSi_3$
Ni_2Si	$NiSi$		

The melting-point of 98 per cent. siliconis about 1420°.

The element burns in oxygen to form silicon dioxide, and is also attacked by chlorine. It does not dissolve in any of the common acids except hydrofluoric acid, and is therefore used extensively in acid-resisting cast iron ; but it is attacked by steam and more rapidly by caustic alkalies, liberating hydrogen,

$$Si + 2KOH + H_2O = K_2SiO_3 + 2H_2\,;$$

this last action is used for preparing hydrogen, especially for military purposes, the silicon being carried in the form of ferrosilicon (see below) and the alkali as a solid.

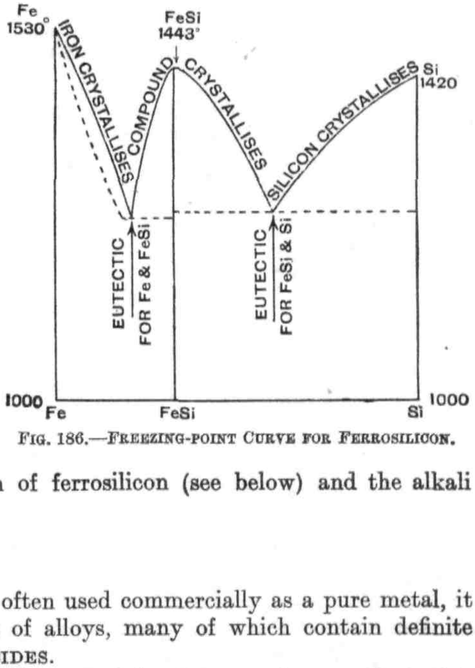


FIG. 186.—FREEZING-POINT CURVE FOR FERROSILICON.

Silicides.

Although silicon is not often used commercially as a pure metal, it forms an important series of alloys, many of which contain definite compounds known as SILICIDES.

(*a*) *Ferrosilicon.*—The silicon used in the manufacture of steel is generally supplied in the form of FERROSILICON. This is an alloy prepared by reducing siliceous iron ore in the electric furnace. The two elements unite to form a compound, FeSi, melting at about 1443°, intermediate between silicon, 1420°, and iron, 1530° (Fig. 186) ; a compound, Fe_2Si, melting at 1250° has been described, but does not appear on the freezing-point curve. Silicon is added to iron

(i) To break up the carbide Fe_3C and convert it into iron and graphite, thus changing white cast iron into grey cast iron (p. 771)

(ii) To improve the magnetic permeability of iron, this action being brought about also by the decomposition of the carbide.

(iii) To produce an acid-resisting alloy.

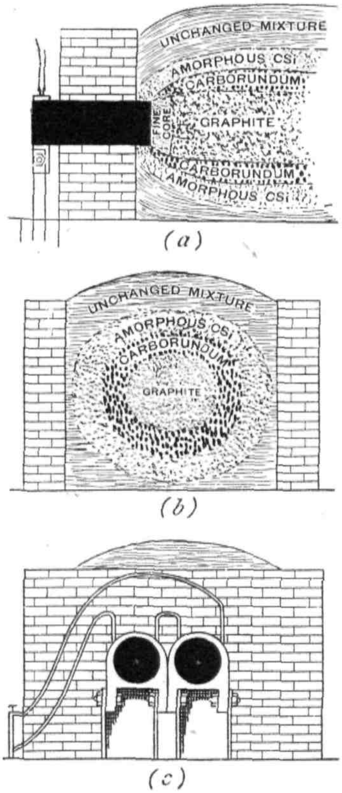


FIG. 187.—ELECTRIC FURNACE FOR MANUFACTURE OF CARBORUNDUM.

(b) *Calcium Silicide*, $CaSi_2$, prepared by reducing a mixture of lime and silica with carbon in the electric furnace, is used instead of aluminium as a constituent of explosives.

(c) *Carbon Silicide*, CSi, is manufactured on a large scale by the reduction of silica with carbon in the electric furnace (Fig. 187),

$$3C + SiO_2 = CSi + 2CO.$$

If heated more strongly, it is decomposed, leaving a residue of graphite (p. 442). It is used as an abrasive under the name of CARBORUNDUM.

The furnace shown in Fig. 187 may be 30 feet long and 10 feet in diameter, *the core of graphite being about 3 feet* in diameter. The ends of the furnace are permanent, but the sides are built up from fireclay blocks. The charge surrounding the core is a mixture of finely-ground anthracite or coke and silver sand, with some sawdust and salt to keep the mass porous and allow the carbon monoxide to escape freely. The current increases gradually from *6,000 to 20,000* amperes and the pressure decreases from 230 to 75 volts during the heating, which occupies a period of about 36 hours. The zone of carborundum thus produced is about 18 to 20 inches thick.

SILICON AND HYDROGEN.

Hydrides of Silicon.

(*a*) **Silicomethane,** SiH_4, *is obtained in a crude state as a colourless, spontaneously-inflammable gas by the action of hydrochloric acid on magnesium silicide* (compare TeH_2, p. 359),

$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4.$$

It is also formed in minute quantities by the direct combination of silicon with hydrogen,

$$Si + 2H_2 \rightleftarrows SiH_4;$$

but this action is a balanced one, since the hydride when heated deposits an opaque mirror of silicon and liberates twice its volume of hydrogen (compare the decomposition of methane by sparking, p. 448).

The gas condenses at a critical temperature of 0°, and under a critical pressure of 100 atmospheres, to a liquid which boils at − 116° under a pressure of 730 mm. It burns readily in air and oxygen, igniting much below a red heat; it also takes fire and burns in chlorine,

$$SiH_4 + 4Cl_2 = SiCl_4 + 4HCl.$$

(*b*) **Silicoethane, Si_2H_6,** is obtained as a by-product of the action of acids on magnesium silicide, but is the main product of the action when lithium silicide, Li_6Si_2, is used.

$$Li_6Si_2 + 6HCl = 6LiCl + Si_2H_6.$$

It is a liquid which boils at + 52° and freezes at − 138°.

It burns spontaneously in air, and forms an explosive mixture with the vapour of carbon tetrachloride,

$$2Si_2H_6 + 3CCl_4 = 4Si + 3C + 12HCl,$$

and with sulphur hexafluoride, SF_6,

$$Si_2H_6 + SF_6 = 2Si + S + 6HF.$$

Silicon and the Halogens.

Silicon Tetrafluoride, SiF_4, is formed by the action of hydrofluoric acid on silica or a silicate,

$$4HF + SiO_2 \rightleftharpoons SiF_4 + 2H_2O$$

It can be prepared by heating a mixture of powdered fluorspar and sand or glass with strong sulphuric acid,

$$2CaF_2 + 2H_2SO_4 + SiO_2 = SiF_4 + 2CaSO_4 + 2H_2O.$$

As the action of hydrofluoric acid on silica is reversible, the sulphuric acid is of value in eliminating water and so preventing decomposition of the silicon tetrafluoride. The gas is also formed by the direct action of fluorine on silicon.

Silicon tetrafluoride is a pungent gas; the solid melts at − 77° under 2 atmospheres pressure to a liquid which boils at − 65° under 1800 mm. pressure; under lower pressures the solid sublimes without liquefying, like carbon dioxide (p. 457) which melts at − 57° and sublimes at − 79° under a pressure of 1 atmosphere. The gas does not burn, but is decomposed by water, forming **silicifluoric acid,** H_2SiF_6 (p. 302). It combines with ammonia to form a white crystalline compound, $SiF_4,2NH_3$, which is decomposed by water; it also unites with phosphine at − 22° and 50 atmospheres pressure to form an unstable crystalline compound, $3SiF_4,2PH_3$.

Silicon Tetrachloride, $SiCl_4$, is produced by the action of chlorine on metallic silicides or on a heated mixture of silica and charcoal,

$$Si + 2Cl_2 = SiCl_4$$
$$2C + SiO_2 + 2Cl_2 = SiCl_4 + 2CO.$$

The by-products of the preparation include a series of "homologues" (p. 448) such as Si_2Cl_6, Si_3Cl_8, Si_4Cl_{10}, Si_5Cl_{12}, and Si_6Cl_{14}, in which the increments between successive members of the series are $SiCl_2$, instead of CH_2.

Silicon tetrachloride is a colourless liquid which boils at 58°; the solid melts at − 89°. It is decomposed by water, giving silicic and hydrochloric acids,

$$SiCl_4 + 3H_2O = H_2SiO_3 + 4HCl,$$

and by potassium, which liberates silicon when heated in the vapour. By the action of sulphur trioxide it gives an oxychloride, $Cl_3Si{\cdot}O{\cdot}SiCl_3$ (contrast phosgene, $Cl{\cdot}CO{\cdot}Cl$, p. 453), and then silica,

$$2SiCl_4 + 2SO_3 = Si_2OCl_6 + S_2O_5Cl_2$$
$$SiCl_4 + 4SO_3 = SiO_2 + 2S_2O_5Cl_2.$$

Silicochloroform, $SiHCl_3$, is prepared by acting on silicon or on metallic silicides with gaseous hydrogen chloride instead of chlorine,

$$Si + 3HCl = SiHCl_3 + H_2$$

(compare the case of tin, where chlorine gives stannic chloride,

$$Sn + 2Cl_2 = SnCl_4,$$

whilst hydrogen chloride gives stannous chloride,

$$Sn + 2HCl = SnCl_2 + H_2;$$

in the case of silicon a molecule of HCl is added to the hypothetical $SiCl_2$).

It is a liquid which boils at 33° and freezes at − 134°. It is not attacked by sodium at 150°, but when heated in sealed tubes with stannic fluoride it exchanges its chlorine for fluorine and gives **silicofluoroform**, $SiHF_3$,

$$3SnF_4 + 4SiHCl_3 = 4SiHF_3 + 3SnCl_4,$$

a gas which when frozen melts at − 110° and boils at − 80°.

Unlike silicon tetrachloride, silicochloroform is inflammable and forms an explosive mixture with nitrogen peroxide; it is also readily oxidised by oxygen, ozone, sulphur trioxide, and chromium trioxide, giving rise to oxychlorides, compare

$$\underset{\text{Chloroform}}{CHCl_3} + O = \underset{\text{Phosgene}}{COCl_2} + HCl.$$

The product is a complex mixture of silicon oxychlorides to which structural formulæ have been assigned as follows:

$$Cl_3Si{\cdot}O{\cdot}SiCl_3$$
$$Cl_3Si{\cdot}O{\cdot}SiCl_2{\cdot}O{\cdot}SiCl_3$$
$$Cl_3Si{\cdot}O{\cdot}SiCl_2{\cdot}O{\cdot}SiCl_2{\cdot}O{\cdot}SiCl_3, \text{ etc.}$$

The principal feature of these compounds is the recurrence of the group $-O \cdot SiCl_2 \cdot O-$. Analogous compounds have also been prepared in which the group $-O \cdot SiPh_2 \cdot O-$ is present (where Ph = C_6H_5), whilst the silicic acids and silicates (see below) contain the group $-O \cdot SiO \cdot O-$.

Bromine and Iodine Compounds corresponding with several of the chlorine compounds described above have also been prepared.

Silicon and Oxygen.

Silica or Silicon Dioxide, SiO_2.

This oxide is by far the most important of the compounds of silicon. It forms about 60 per cent. of the solid crust of the earth, the remaining 40 per cent. consisting mainly of basic oxides of the metals; the proportion of silica is so large that when the basic oxides have united with a maximum proportion of silica there is still a residue of about 12 per cent. of silica uncombined.

Silica can be obtained in an amorphous form with and without water and in not less than three crystalline forms.

(*a*) *Amorphous Silica* can be prepared from the crystalline forms by fusion; the liquid is of such high viscosity that it will not flow unless heated considerably above its melting-point; incipient fusion is therefore generally indicated only by the sintering of the powder or by the rounding of the sharp edges of a crystal. Under these conditions, it is not surprising that the product solidifies in a glassy form without undergoing crystallisation. At temperatures slightly above the melting-point, silica vaporises rapidly. Silica-glass has the following properties:

(i) It does not begin to soften until it is heated to 1500°, although it crystallises on prolonged heating at about 1200°.

(ii) Its density, 2·2, is less than that of the crystalline forms of quartz.

(iii) Its coefficient of expansion is very small, less than 1/1,000,000 per degree. It is therefore very resistant to sudden changes of temperature, *e.g.*, it can be heated to redness and quenched in water without fracture. For this reason silica-glass is specially suited for experiments in which a transparent glass is required which will stand very high temperatures and rapid changes of temperature. It is also possible by using silica-glass to build up large and complex pieces of apparatus, which could not be constructed of ordinary glass without flying to pieces.

(iv) It is quite free from alkali and very resistant to attack by acids. It can therefore be used for delicate chemical operations in which complete freedom from alkalies is required,

as well as commercially for condensing nitric acid and for concentrating sulphuric acid.

(v) It is very transparent, not only to visible light, but also to ultra-violet and infra-red radiations.

(*b*) *Crystalline Silica* exists in three forms,

(i) QUARTZ, stable up to 870°, density 2·65.*

(ii) TRIDYMITE, stable from 870° to 1470°, density 2·3, melting-point 1670° if not previously changed into cristobalite.

(iii) CRISTOBALITE, stable from 1470° to its melting-point at 1710°, density 2·3.

These crystalline forms are not readily converted into one another, and in particular tridymite has persisted as a mineral without reverting to the more stable form of quartz. The transition-temperatures were determined by heating the material for several hours in an electric furnace, either alone or in presence of a solvent such as sodium tungstate and noticing at what temperatures changes of crystalline form occurred.

Quartz may occur

(i) As a primary mineral in granite and other igneous rocks rich in silica, in which it is usually the last constituent to crystallise and is therefore particularly rich in liquid and gaseous inclusions.

(ii) As sand or sandstone, a final residue from the decomposition of igneous rocks by water, persisting in a granular form on account of its hardness and chemical inactivity.

(iii) As a crystalline deposit from aqueous solutions, *e.g.*, in mineral veins and as a cementing material in sedimentary rocks.

Tridymite is almost unknown in deep-seated igneous rocks, but is found in lavas which have crystallised under smaller pressure.

Cristobalite is an even less common form of the oxide.

(*c*) *Properties of Quartz.*—QUARTZ OF ROCK-CRYSTAL (Fig. 188) is so perfect an example of crystallisation that it has given its name to the whole group of CRYSTALS (Greek, κρύσταλλος, ice). On account of its great hardness it is used for making lenses, whilst its transparency to infra-red and ultra-violet light makes it a most valuable material for lenses and prisms in optical apparatus. The crystals are of special interest on account of the fact that they have no plane or centre of symmetry, and can therefore exist in two forms (Fig. 189), which rotate the plane of polarisation of a beam of light passing along the principal (3-fold) axis of the crystal in the one case to the right and in the other case to the left.

* Quartz has no definite melting-point, as it always begins to change into cristobalite before it melts.

Quartz which has been heated above 575° changes into a β-form which on etching gives markings of a different pattern from those of ordinary or α-quartz. It is therefore possible to use quartz as a "geologic thermometer"; thus, vein-quartz has been deposited below 575°, and is in the α-form, but the quartz-crystals in granite have crystallised out above 575° and are in the

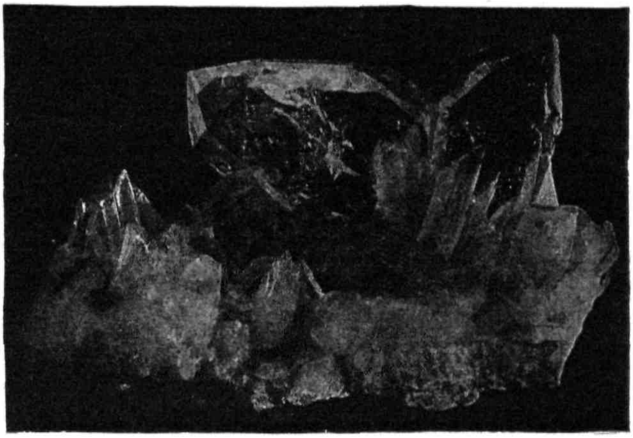
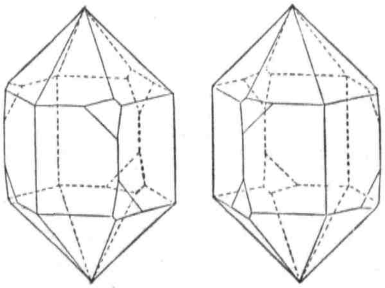


FIG. 188.—CRYSTALS OF QUARTZ.
(British Museum, Natural History.)

β-form. In view of the fact that most rocks crystallise above 1000° it is remarkable that quartz, which is only stable up to 870°, is so common, and tridymite, which is stable from 870° to 1470°, so rare in igneous rocks. This may be accounted for, not merely by a secondary conversion of tridymite into quartz by recrystallisation during cooling, but also



(a) Right-handed. (b) Left-handed.
FIG. 189.—CRYSTALS OF QUARTZ.

(i) By the presence of about 1·5 per cent. of water, which is a normal constituent of deep-seated igneous rocks, and would have an important influence in lowering the temperature of crystallisation.

(ii) By the influence of pressure, which would raise the temperature of crystallisation, since crystalline silica is denser than amorphous silica, but would have a still more marked effect in raising the temperature of conversion of tridymite into quartz, since this change is accompanied by a still larger contraction, the densities in question being as follows:

Amorphous silica	2·2
Tridymite	2·3
Quartz	2·65

The absence of pressure during the crystallisation of lavas would therefore promote the formation of tridymite instead of quartz, as is actually observed.

(*d*) *Chemical Properties of Silica.*

(i) Silica is almost insoluble in water and does not act on indicators; but it dissolves in alkalies, forming a series of SILICATES (see below). Tridymite, unlike quartz, is dissolved by sodium carbonate, either fused or in aqueous solution, as well as by sodium hydroxide. Mixtures of silicates, prepared by melting sand with alkalies and earths, are manufactured as GLASS (p. 496); silicates are also present in CLAY (and therefore in bricks, earthenware, pottery, and porcelain) and in PORTLAND CEMENT (p. 640).

(ii) Silica is not attacked by acids, with the exception of hydrofluoric acid; this converts it into the gaseous silicon fluoride, SiF_4 (p. 489), so that silica can be vaporised completely by treatment with hydrofluoric acid.

(iii) When heated in the electric furnace with sufficient carbon to remove only one-half of the oxygen (contrast preparation of silicon, p. 486), silica is converted into **silicon monoxide,** SiO,

$$SiO_2 + C = SiO + CO.$$

This is a brown powder of density 2·2, and is used as a pigment under the name of MONOX.

Silicic Acid.

Silicic Acid, SiO_2,xH_2O, is the acid of which silica is the anhydride. It has not been isolated in a crystalline form, but is usually obtained as a jelly containing very variable proportions of water. **Gelatinous silicic acid** is produced by the action of acids on a soluble silicate, *e.g.*,

$$Na_2SiO_3 + H_2SO_4 = H_2SiO_3\ aq. + Na_2SO_4.$$

It can be retained in solution in a colloidal form and separated from soluble salts by diffusion through parchment, which retains the colloidal acid but allows the "crystalloid" salts to escape. The colloidal solution, which is tasteless and has a slight acid reaction, coagulates readily, especially in presence of salts of multivalent metals, *e.g.*, aluminium salts are more effective than salts of magnesium and calcium, and these in their turn are more effective than salts of sodium and potassium in precipitating the acid. Soluble or colloidal silicic acid is probably formed also when mineral silicates are decomposed by carbonic acid, and from such solutions the silicic acid may be deposited in an amorphous form, *e.g.*, as OPAL, containing from 0 to 30 per cent. of water, the normal proportion being from 5 to 10 per cent. The deposition of the silica, unlike that of dissolved chalk, does not depend on loss of carbon dioxide, but on the coagulation of a colloid. The conditions under which this takes place are more complex, and the colloidal character of the solution is probably responsible for the local deposition of amorphous silica around nuclei of organic matter in beds of chalk; these local deposits have hardened into FLINTS, which have the density of quartz, although their crystalline character is not

otherwise obvious. The spicules of sponges consist very largely of opaline or hydrated silica and can often be detected in flint. INFUSORIAL EARTH consists almost entirely of the siliceous remains of diatoms, and similar materials when consolidated into rock are described as CHERT.

Whilst there is no clear evidence to show that crystallised silica can be converted directly into silicic acid, the reverse change takes place very readily. Thus, the whole of the quartz contained in mineral veins has probably been deposited from aqueous solutions of silicic acid; crystals of quartz may also be detected in flint, and AGATE (Fig. 182), which is remarkable for its banded structure, is a micro-crystalline form of silica, deposited in successive layers in cavities of decomposing igneous rocks. These amorphous or microcrystalline forms of silica are quite as hard as the ordinary crystals of quartz; agate mortars are therefore used for grinding minerals for analysis, and chipped flints provided the earliest tools and weapons in almost every region in which the remains of primitive man have been found.

Metallic Silicates.

Metallic silicates are difficult to prepare artificially, mainly because they melt to viscous liquids, which crystallise with extreme slowness even under the most favourable laboratory conditions. For this reason the study of silicates has been confined almost entirely to natural minerals. Silicates of the alkalies are, however, soluble in water and can be crystallised from it, and a few simple silicates have been prepared in a crystalline form by direct combination of the constituent oxides. Experiments have also been made to prepare various minerals artificially and to detect them as constituents of slags and other artificial products.

The readiness with which crystallisation of a silicate takes place depends on the nature and proportion of the bases with which the silica is combined; it increases with the proportion of base and decreases as the complexity of the mixture is increased. Thus, **potassium metasilicate**, K_2SiO_3, cannot be crystallised even by slow cooling; the corresponding **sodium silicate**, Na_2SiO_3, crystallises if cooled slowly, but can be obtained as a glass by cooling rapidly, whilst **lithium silicate**, Li_2SiO_3, was for a long period known only in the crystalline form. In the same way, **lead silicate**, $PbSiO_3$, solidifies as a glass, whilst **barium silicate**, $BaSiO_3$, and **calcium silicate**, $CaSiO_3$, crystallise readily; the latter compound can be prepared as a glass by quenching it in water, but the more basic **calcium orthosilicate**, Ca_2SiO_4, cannot be fixed as a glass in this way. Amongst the more complex silicates, ANORTHITE, $CaAl_2Si_2O_8$, crystallises fairly readily at 1550°, but the isomorphous sodium compound ALBITE, $NaAlSi_3O_8$, which melts at about 1250°, gives such a viscous product that it is almost impossible to determine the melting-point accurately.

The properties of the simple silicates are described in Parts III and IV under the metals from which they are derived, but those of the

glasses and of the silicate-minerals, which usually contain several metals, are summarised in the following paragraphs.

Glass.

The ordinary forms of glass are complex mixtures of silicates, in some cases with borates, and in some optical glasses with phosphates of various metals. The bases include the oxides of calcium, lead, barium, zinc, magnesium, aluminium, sodium, and potassium. Oxides of iron may be present as an impurity, and oxides of cobalt, copper, chromium, etc., may be added for the purpose of producing colour. The glass may thus contain a large number of simple silicates (or borates or phosphates) such as **sodium metasilicate**, Na_2SiO_3, **calcium metasilicate,** $CaSiO_3$, corresponding to the mineral wollastonite (p. 640), **barium disilicate,** $BaSi_2O_5$, **lead metasilicate,** $PbSiO_3$, etc., and also complex silicates such as $2Na_2SiO_3,3CaSiO_3$ and $Na_2Si_2O_5,BaSiO_3$. The essential property of a glass is that it solidifies gradually, *without crystallising,* to a transparent amorphous mass, which is completely " isotropic " (p. 4), *i.e.*, which exhibits similar properties in all directions. The viscosity of the glass shows no abrupt increase during cooling; the glass therefore passes through a plastic stage in which it can be shaped either by pressing or blowing, or it may be allowed to solidify and then reheated without showing any tendency to crystallisation. When, however, the mixture of silicates contains some constituent in excess, this may be deposited during the cooling process, giving rise to crystallisation or DEVITRIFICATION (see Frontispiece); thus calcium sodium silicates having a high percentage of calcium tend to deposit **calcium metasilicate**, $CaSiO_3$, whilst those rich in silica tend to deposit free **silica**, SiO_2. Even when crystallisation does occur, the term " glass " may still be employed; for example, opal glass frequently owes its special characteristics to the presence of minute crystals, *e.g.*, of silica in " alabaster glass."

Composition of Glass.

For convenience, the different types of glass may be classified broadly as follows :—

(*a*) *Glass for Common Pressed or Blown Ware.*

This type of glass consists mainly of silica (65 to 78 per cent.), soda (11 to 18 per cent. Na_2O), and lime (5 to 18 per cent.). The fusibility of the glass increases with the proportion of Na_2O which it contains, and, conversely, the difficulty of melting increases as the amount of CaO or SiO_2 is increased. Its density is 2·4 to 2·6, and its refractive index $\mu_D = 1{\cdot}5$ to 1·53. Besides soda and lime, bases such as magnesia and alumina may be present in amounts varying from 0·5 to 4 per cent.; the alumina may be present either as an accidental impurity derived from the raw materials, or from parts of the furnace, or may be added deliberately either as a definite basic constituent or in order to hinder devitrification. Baryta may also be used to some extent to replace the lime for certain types of pressed glass when increased brilliance and density are required.

The soda-lime glasses are employed for a very large number of purposes, *e.g.*, as BOTTLE-GLASS, for glass containers of all kinds, for PLATE-GLASS, WINDOW GLASS, and for the well-known type of optical glass known as CROWN-GLASS.

(*b*) *Glasses containing Lead.*

The lead glasses are characterised by a low softening point and a slow change of viscosity, enabling them to be worked while hot over quite a wide range of temperatures. Further, their density and refractive index are both high. Lead glasses containing a high percentage of lead oxide are not readily attacked by boiling water or by acids, but are more easily affected by alkalies ; the resistance of the glass is, however, greatly increased by the presence of a small amount of boric oxide.

A lead-potash glass containing 30 to 35 per cent. of PbO is used for the best English crystal glass and for imitation gem-stones. Lead-soda glass containing from 18 to 30 per cent. of PbO, and sometimes a little potash or alumina or boric oxide, is employed on a large scale for making electric light bulbs and for the glass tubing and rod which are sealed to the bulb.

(*c*) *Scientific and Heat-resisting Glass.*

Such glass may contain a number of different constituents, each added for a certain specific purpose. (i) Resistance to attack by water and by aqueous solutions may be brought about by increasing the proportions of silica, boric oxide, alumina, and zinc oxide in the glass. Resistance to acids is increased by increasing the proportion of silica, alumina, and lime in a glass ; on the other hand, a glass containing much silica does not offer a satisfactory resistance to alkaline solutions. A glass which is to be resistant to all types of chemical agents is, therefore, a compromise, and widely different types of glass have been used for chemical purposes. JENA CHEMICAL GLASS contains boric oxide, zinc oxide, and some alumina, with silica. On the other hand, PYREX GLASS contains 80 per cent. of silica, 12 per cent. of boric oxide, and small amounts of soda and alumina. The best samples of chemical ware usually contain silica, lime, zinc oxide, alumina, and boric oxide, with soda.

(ii) Glass for lampworking (scientific glass-blowing) contains silica, lime, alumina, potash, and soda ; thus, one very good glass has the composition

SiO_2	Al_2O_3	CaO	K_2O	Na_2O
69	3	7	6·5	14·5 per cent.

(iii) BOHEMIAN GLASS contains potash and lime, although a resistant glass is obtained by using a mixture of potash and soda with lime. The modern heat-resisting glasses are all practically of the same type as those used for chemical ware, since alumina, magnesia, zinc oxide, and boric oxide not only bestow resistance to weathering, but also reduce the coefficient of expansion of the glass. Heat-resisting glasses usually have also a high softening point and are used for combustion tubes, lamp-glasses and illuminating ware, and cooking utensils.

(*d*) *Optical Glass.*

There is no general formula for OPTICAL GLASS, since such glass has no peculiar composition, except that glasses containing phosphoric oxide can be used for lenses occupying protected positions in an optical instrument. These phosphate glasses would be useless for other types of article, since they are readily attacked by water and by acids. Optical glasses contain just those constituents which will give the desired refractive index and

dispersion, provided that the glass is resistant to weathering and can be cooled slowly without devitrification. All the types of glass already mentioned may, therefore, find employment in optical instruments. Where the glass is mainly a lime-soda glass, it is known as CROWN GLASS. If the glass contains barium instead of lime, it is described as a BARIUM CROWN GLASS, or if zinc is present, as a ZINC CROWN GLASS. Glasses containing lead are known as FLINT GLASS; they are distinguished as light, medium, dense, or extra dense flints, according to the proportion of lead oxide which they contain. Borosilicate glasses also occupy an important position in the list of optical glasses.

(e) *Coloured Glasses.*

(i) Coloured glass may be produced by the addition of some substance which forms a coloured silicate, *e.g.*, cobalt oxide, which even in very small quantities gives an intense blue colour to the glass. In the same way copper oxide under oxidising conditions gives a blue colour, and chromium oxide gives a vegetable-green colour.

(ii) Colour may also be produced by introducing into the glass minute colloidal particles of some insoluble substance. Thus RUBY GLASSES are produced by very small quantities of copper, gold, or selenium, added in the form of a salt, together with a reducing agent. Such glasses are usually colourless or only slightly coloured when melted, but on reheating in the neighbourhood of the annealing or softening temperature develop a red colour. Carbon and sulphur produce amber colours. It has been suggested that the colour of ultramarine (p. 662) is of this type.

(iii) In the preparation of glass, the presence of small amounts of iron oxide, either in the sand or in other raw materials, leads to a green colour. In order to produce white glass a decoloriser is needed, manganese dioxide being largely used in lead glasses (0·2–0·4 part per 100 parts of sand) and selenium in tank furnaces where reducing conditions exist. These two substances alone produce a colour in the glass which is complementary to that of the green ferrous silicate.

The Melting of Glass.

Glass may be melted either in a pot-furnace or in a tank-furnace.

(a) *Pot-Furnaces.*—In a pot-furnace, the materials are charged into a crucible of fireclay which may be covered or may have an open top. The furnace may hold from 2 to 18 pots and each pot may contain from 3 or 4 cwts. up to 30 to 35 cwts. Modern furnaces are heated by producer gas, the temperature being increased and fuel economised either by REGENERATIVE HEATING (Fig. 190, compare p. 764 and Figs. 168, 192, 260 and 282) or by a system of RECUPERATION (Fig. 191, compare p. 468 and Fig. 178) in which the air on its way to the combustion chamber passes through clay pipes and is heated continuously by the hot gases escaping from the furnace. Pot-furnaces are employed for the better qualities of glass, including optical glass, table glass, etc.

In Fig. 190, the gas and air on the way to the furnace are heated regeneratively by brickwork made hot by the burnt gases passing to the chimney: two series of flues are provided and the direction of flow of the gases is reversed at short intervals by reversing valves as shown in the figure.

In Fig. 191, *P* is the gas-producer, *GP* is the glass-pocket into which the glass can fall, in case a pot should break, *B* is the flue through which secondary air (p. 240) enters the combustion-chamber, after passing through the "recuperators" marked *R*.

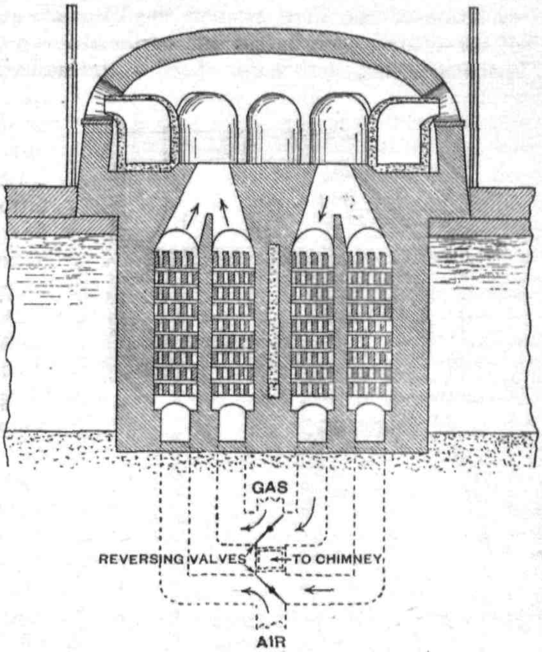


Fig. 190.—Glass-pot Furnace with Regenerative Heating.

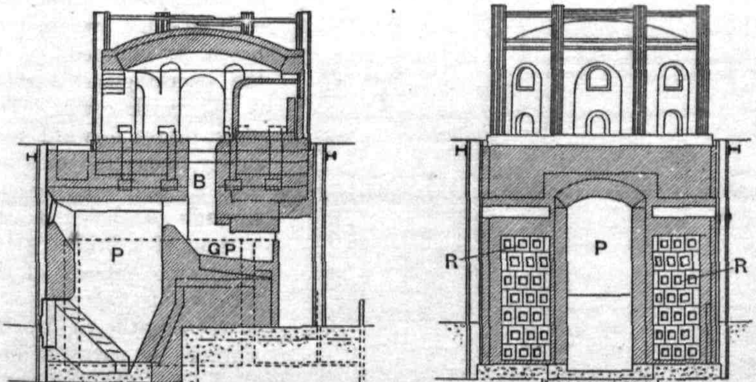


Fig. 191.—Glass-pot Furnace with Recuperative Heating of Secondary Air.

(*b*) *Tank-furnaces.* — Window glass, bottle glass, and certain types of cheap domestic glassware are melted in tank-furnaces, which may hold anything from two or three tons up to 500 tons. Fig. 192 shows such a furnace. Practically all such furnaces are worked on the regenerative system and heated by producer gas, although in a few cases oil burners are employed.

(*c*) *Melting.*—The mixture from which the glass is to be produced is called the "batch." In the first stage of fusion there is a violent evolution of gas, since most of the bases are introduced in the form of carbonates, such as calcium carbonate, sodium carbonate, barium carbonate, zinc carbonate. Lead is introduced, however, either as red lead or as litharge, and sodium may also be introduced as salt-cake, Na_2SO_4, or as sodium nitrate, $NaNO_3$. After the first stage of chemical action, the temperature of a pot-furnace is allowed to rise in order that the melted glass may become mobile and enable bubbles of gas to escape. When these have been removed, the glass is said to be "plain," and is ready for working after the temperature has again been reduced slightly so as to give the glass sufficient viscosity. In the case of a tank-furnace there is a permanent gradient of temperature from the melting-end, where the batch is charged in, to the working-end, where it is withdrawn. The glass passes forward very slowly, from the melting-end to the working-end, through a hole at the bottom of a bridge which divides the interior of the furnace into two parts. It is then gathered by the workers by means of long hollow iron pipes, and in most cases is rolled first into the shape of a hollow cylinder and then blown out into a mould or worked up in some other suitable form. Much of the common glassware is, however, now made by machinery, some of which does not require the interposition of the glass-worker.

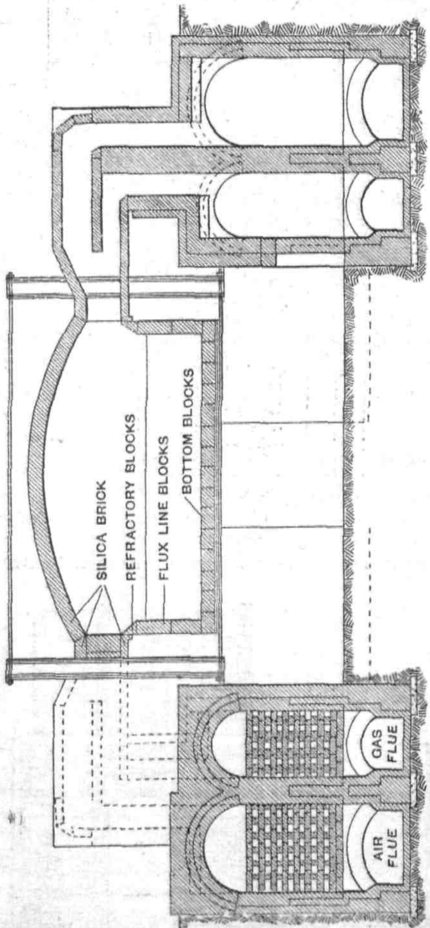


FIG. 192.—Cross-section of Tank-furnace with Regenerative Heating.

Mineral Silicates.

(*a*) *Nomenclature.*—The principal difficulty in gaining a general impression of the mineral silicates arises from the bewildering nomenclature which has been adopted by mineralogists in describing the so-called MINERAL SPECIES. It has already been pointed out that mineral silicates are usually isomorphous mixtures; the vicarious replacement of one element by another may have a marked effect on the properties of the mineral, and it is not unusual for a series of isomorphous compounds to be divided up into several species (shading imperceptibly into one another) according to the proportions in which the different isomorphous metals are present. A further complexity arises from the fact that isomorphism in the silicates may result, not merely in a simple replacement of aluminium by ferric iron or of magnesium by ferrous iron, but in the blending of compounds of dissimilar formulæ and composition, as in the case of the felspars and micas. The attempt to differentiate between various typical mixtures of isomorphous compounds and to distinguish their ideal pure components from actual crude minerals has led to an array of names which even a mineralogist can scarcely be expected to carry in his memory.

(*b*) *Alumino-silicates.*—After silica, which forms 60 per cent. of the earth's crust, the commonest oxide is alumina, which is present to the extent of about 15 per cent. Most of the mineral silicates therefore contain alumina, usually combined with one of the three stronger bases, soda, potash, and lime, which represent about 11 per cent. of the earth's crust; a part of the alumina may be replaced by ferric oxide (2·7 per cent.), and in some cases the basic constituent may be replaced in part or wholly by water (2·0 per cent. of the earth's crust). Alumino-silicates have been described as SALIC (*i.e.*, Si + Al) MINERALS and are conveniently classified according to the ratios of silicon to aluminium which they contain.

(*c*) *Ferromagnesian Silicates.*—The second important group of silicates consists mainly of isomorphous mixtures of magnesium and ferrous silicates, the two bases MgO and FeO representing 3·7 and 3·4 per cent. of the lithosphere respectively. It is noteworthy that the lime in igneous rocks is usually found as an alumino-silicate, whilst the more feebly basic magnesia appears in the group of ferromagnesian or FEMIC (Fe + Mg) MINERALS. The most important association of these two bases is a definite chemical compound, DIOPSIDE, $MgCa(SiO_3)_2$, compare dolomite, $MgCa(CO_3)_2$. The silicates of the ferromagnesian class include

(i) ORTHOSILICATES, such as Mg_2SiO_4, derived from orthosilicic acid, H_4SiO_4.

(ii) METASILICATES, such as $MgSiO_3$, derived from metasilicic acid, H_2SiO_3.

Alumino-silicates.

The most important classes are :

(1) Trisilicates, *e.g.*, $KAlSi_3O_8$, Al : Si = 1 : 3.
(2) Disilicates, *e.g.*, $KAlSi_2O_6$, Al : Si = 1 : 2.
(3) Monosilicates, *e.g.*, $KAlSiO_4$, Al : Si = 1 : 1.

Of these compounds, the trisilicates are by far the most important, their formation being favoured by the enormous excess of silica in the crust of the earth. They are specially abundant in deep-seated igneous rocks, where pressure appears to favour the combination of a maximum amount of silica with the bases, although even there the lime usually separates as an alumino-monosilicate. In lavas, on the other hand, the potash may appear as a disilicate, $KAlSi_2O_6$, and the soda as a monosilicate, $NaAlSiO_4$, especially if the lava is relatively poor in silica.

Alumino-trisilicates : The Felspars.

Nearly 60 per cent. of the igneous rocks of the earth's crust is composed of FELSPARS.

(*a*) **Potash-felspar,** or **potassium alumino-trisilicate,** $KAlSi_3O_8$, crystallises as ORTHOCLASE, in the *monosymmetric* system with one plane

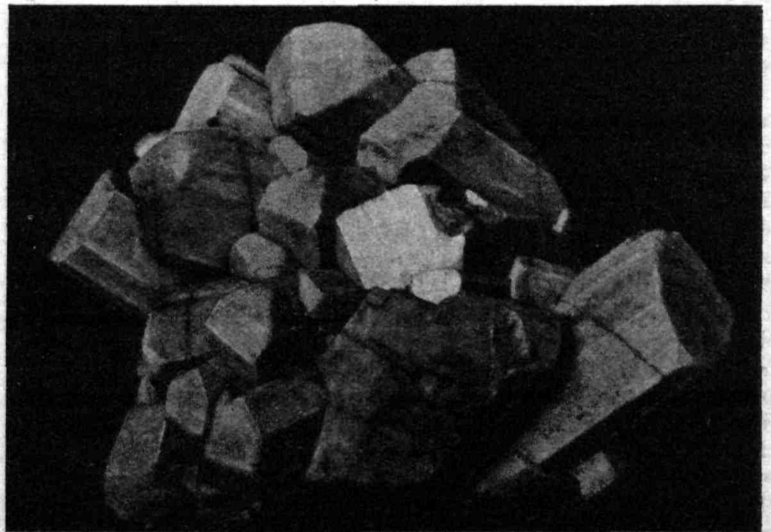


FIG. 193.—MICROCLINE OR POTASH-FELSPAR (ANORTHIC FORM). × $\frac{2}{3}$. (British Museum, Natural History.)

of symmetry. It is often stained yellow or red by the presence of iron, and it may retain its monosymmetric symmetry even when more than half of the potash has been replaced by soda. Potash felspar is,

however, dimorphous and is found also in *anorthic* crystals, which have no plane of symmetry and correspond with one form of soda-felspar; these are described as MICROCLINE (Fig. 193); monosymmetric crystals of orthoclase are seen in Figs. 183 and 201.

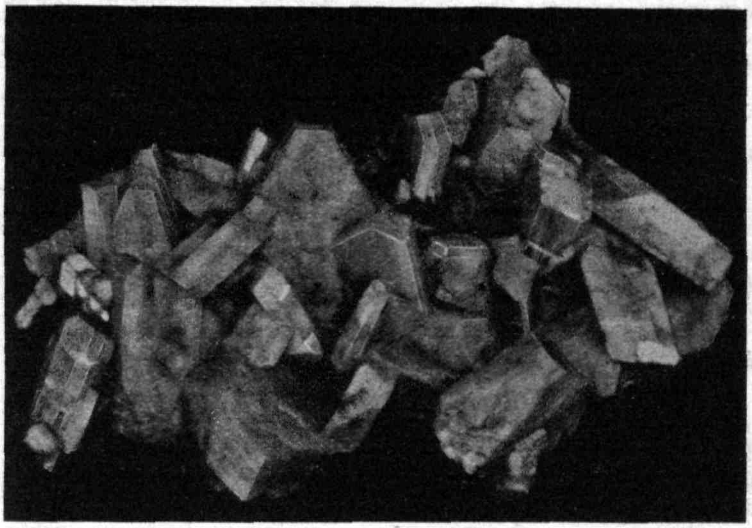


FIG. 194.—ALBITE OR SODA-FELSPAR (ANORTHIC). × ¾. (British Museum, Natural History.)

(*b*) **Soda-felspar,** or **sodium alumino-trisilicate,** $NaAlSi_3O_8$, crystallises in the *anorthic* system as ALBITE (Fig. 194). Crystals isomorphous with microcline and often containing potash as well as soda are described as ANORTHOCLASE.

(*c*) **Lime-felspar,** or **calcium alumino-monosilicate,** $CaAl_2Si_2O_8$, is a monosilicate corresponding with the sodium compound $NaAlSiO_4$; but it crystallises as ANORTHITE in the *anorthic* system and forms a complete series of isomorphous mixtures with soda-felspar or albite, $NaAlSi_3O_8$. The isomorphism of these minerals has been proved by studying the melting-points of mixtures of the two pure compounds $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$

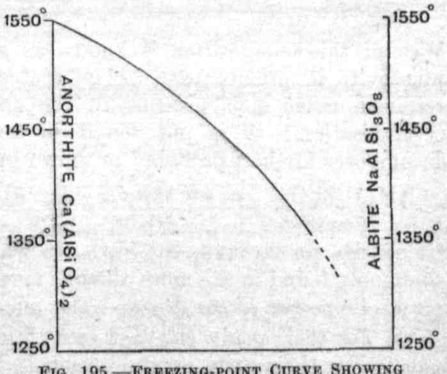


FIG. 195.—FREEZING-POINT CURVE SHOWING ISOMORPHISM OF ALBITE AND ANORTHITE.

(Fig. 195) ; the melting-point of the lime-felspar is 1550°, but this is lowered progressively to about 1250° by the addition of soda-felspar, although the mixtures rich in soda form such viscous liquids that it is almost impossible to determine their melting-points correctly. The isomorphism of these two compounds may be compared with that of sodium nitrate and calcium carbonate, since the sum of the valencies of the oxides is constant in each pair of compounds, thus :

$Ca\ Al_2\ Si_2O_8$			$Ca\ CO_3$		
$2+6+8$	=	16	$2+4$	=	6
$Na\ Al\ Si_3O_8$			$Na\ NO_3$		
$1+3+12$	=	16	$1+5$	=	6

Lime-felspar may also have part of its lime replaced by soda according to the ordinary law of vicarious replacement, indicating the presence of an asymmetric form of sodium alumino-monosilicate, $NaAlSiO_4$ or $Na_2Al_2Si_2O_8$, compare $CaAl_2Si_2O_8$.

Synthesis and Decomposition of Felspars.

(*a*) *Synthesis of Felspars.*—Lime-felspar can be synthesised easily from its component oxides, since the molten mass crystallises readily. The alkali felspars usually give glassy products, but soda-felspar can be crystallised by melting it with half its weight of magnetite, Fe_3O_4, and both soda and potash felspars can be crystallised by heating strongly in presence of a solvent, *e.g.*, a molten tungstate, phosphate, fluoride, or silicofluoride.

(*b*) *Decomposition of Felspars.*—Felspar can be converted into MICA by the action of water and carbon dioxide, which eliminate two-thirds of its potash as potassium carbonate and two-thirds of its silica in the form of quartz, and thus change the alumino-trisilicate into an alumino-monosilicate, $KH_2(AlSiO_4)_3$, as shown in the equation

$$\underset{\text{Felspar}}{3KAlSi_3O_8} + H_2O + CO_2 = \underset{\text{Muscovite}}{KH_2Al_3Si_3O_{12}} + \underset{\text{Quartz}}{6SiO_2} + K_2CO_3.$$

Mica of this composition is known as MUSCOVITE. The presence of muscovite in granite may be attributed to the influence of water retained under high pressure in the magma at the temperature of crystallisation ; it is not found in lavas, since when heated it decomposes further, probably as shown in the equation

$$\underset{\text{Muscovite}}{KH_2Al_3Si_3O_{12}} = \underset{\text{Leucite}}{KAlSi_2O_6} + Al_2O_3 + SiO_2 + H_2O,$$

giving rise to LEUCITE, $KAlSi_2O_6$, in which form the potash is very commonly found in the more alkaline lavas.

(*c*) *Properties of the Micas.*—The micas are remarkable

(i) For their ready cleavage into thin elastic sheets (Fig. 3).

(ii) For their early crystallisation in igneous rocks, following that of zircon and apatite and preceding that of felspar and quartz.

(iii) For their resistance to weathering.

(iv) For the isomorphism of dissimilar types of mica (compare soda-felspar and lime-felspar), *e.g.*,

MUSCOVITE, $KH_2Al_3Si_3O_{12}$ (Fig. 196),

is isomorphous with the magnesian micas,

PHLOGOPITE, $KH_2Mg_3AlSi_3O_{12}$ (Fig. 197),

in which Mg_3 has replaced Al_2, and

BIOTITE, $KHMg_2Al_2Si_3O_{12}$,

in which Mg_2 has replaced AlH in muscovite, and with

LEPIDOLITE, $[K,Li]_3(AlF_2)Si_3O_8$,

a fluoriferous mica the formula of which may be derived from that of orthoclase, $KAlSi_3O_8$, by inserting the univalent group AlF_2 in the place of the alkali of the felspar, whilst the aluminium atom is replaced by Li_3.

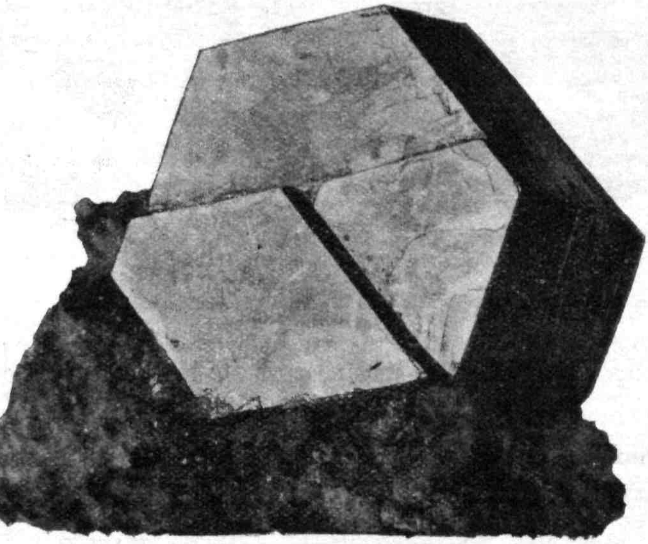


FIG. 196.—MUSCOVITE MICA.
× ¾. (British Museum, Natural History.)
Notice the brilliant cleavage of the six-sided prism of mica.

(*d*) *Formation of Kaolinite.*—A further decomposition in which the whole of the potash of the felspar is eliminated, with two-thirds of the silica, gives rise to a mixture of KAOLINITE and quartz as shown in the equation

$$\underset{\text{Felspar}}{2KAlSi_3O_8} + 2H_2O + CO_2 = \underset{\text{Kaolinite}}{H_4Al_2Si_2O_9} + 4SiO_2 + K_2CO_3$$

Mixtures of mica and quartz or kaolinite and quartz, which have been

formed by the weathering of felspar, and in which the contours of the original crystals of felspar can sometimes be seen, are used extensively

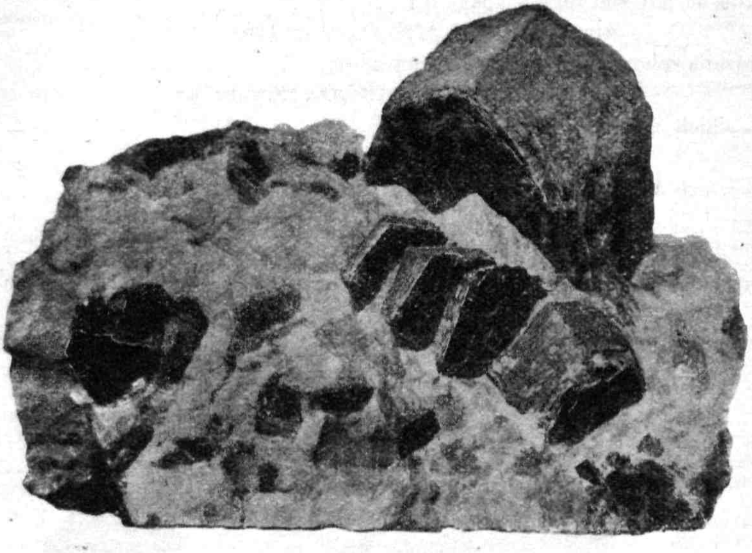


FIG. 197.—PHLOGOPITE MICA.
$\times \frac{3}{4}$. (British Museum, Natural History.)
Notice the shearing of the mica.

in making porcelain. Kaolin is profoundly altered by heat, probably decomposing into a simple aluminium silicate as shown in the equation

$$H_4Al_2Si_2O_9 = Al_2SiO_5 + SiO_2 + 2H_2O.$$

Alumino-disilicates.

(*a*) *Leucite and Analcite.*—Two of the most important disilicates, namely,

(i) **Potassium alumino-disilicate** or LEUCITE, $KAlSi_2O_6$,

(ii) **Sodium alumino-disilicate** or ANALCITE, $NaAlSi_2O_6,H_2O$,

both crystallise in the cubic system, in spite of the fact that the sodium compound contains a molecule of water that is absent in the case of the potassium salt. The two compounds also show a close chemical relationship to one another, since both yield the same anhydrous **ammonium alumino-disilicate,** $NH_4AlSi_2O_6$, when heated in sealed tubes with the vapour of ammonium chloride.

Leucite, which can be synthesised by melting together its constituent oxides, takes up a molecule of water and is converted into analcite when the potash is replaced by soda by heating the mineral at 180° in an aqueous solution of sodium chloride or sodium carbonate.

Conversely, analcite loses its water when it is converted into leucite by similar treatment with potassium salts.

Leucite is a common constituent of lavas, but it is not often found in deep-seated igneous rocks. Analcite, on the other hand, is formed as a primary deposit in the more alkaline deep-seated rocks, where crystallisation has taken place under pressure so as to retain the water, but in superficial rocks it is a secondary product.

(*b*) *The Zeolites.*—Analcite is a member of the group of ZEOLITES or hydrated silicates, which liberate water and boil up when heated by a blowpipe (Greek ζέω, I boil). The water of crystallisation of the zeolites can be driven off without destroying the structure of the crystals, although they usually become opaque during this process. The transparency of the crystals can be restored and their original optical properties reproduced by exposure to moisture. In the case of analcite these results can be explained by assuming the existence of an anhydrous alumino-silicate, $NaAlSi_2O_6$, corresponding with leucite, and isomorphous with its own hydrate, $NaAlSi_2O_6,H_2O$.

Artificial zeolites are used under the name of PERMUTITE for softening water. The original sodium compound removes magnesium and calcium from hard water, forming a magnesium or calcium alumino-silicate ; this can be reconverted into the original sodium compound and rendered available for further use, by acting on it from time to time with a solution of common salt, and washing away both the excess of salt and the calcium and magnesium chlorides which are set free by it.

(*c*) *Jadeite.*—The hypothetical cubic mineral $NaAlSi_2O_6$, analogous to $KAlSi_2O_6$, is only known in the form of dehydrated crystals of analcite ; the actual mineral of this composition, known as JADEITE, is much less symmetrical, crystallising in the monosymmetric system with only one plane of symmetry. It is a tough, green mineral, capable of taking a high polish, and was used by primitive man as an alternative to flint in the manufacture of axes, etc. It is isomorphous with diopside, $MgCaSi_2O_6$ (pp. 620 and 623), just as albite, $NaAlSi_3O_8$, is isomorphous with anorthite, $CaAl_2Si_2O_8$ (p. 504).

Alumino-monosilicates.

(*a*) After lime-felspar or anorthite, $Ca(AlSiO_4)_2$, and muscovite, $KH_2(AlSiO_4)_3$, the most important of the alumino-monosilicates is **sodium alumino-monosilicate**, or NEPHELITE, $NaAlSiO_4$; but analogous compounds, $KAlSiO_4$ and $LiAlSiO_4$, are also found, as well as isomorphous mixtures containing both sodium and potassium. Nephelite, which always contains potassium as well as sodium, and is perhaps more complex than the formula $[Na,K]AlSiO_4$ would indicate, is an important constituent of igneous rocks containing more soda than is required to produce felspar. It can be prepared readily from its constituent oxides and is frequently found in the more alkaline lavas.

(*b*) Sodalite, in which nephelite is combined with sodium chloride, is typical of an interesting group of double salts, which includes the four compounds

$$3NaAlSiO_4,NaCl \qquad 3NaAlSiO_4,Na_2SO_4$$
$$3NaAlSiO_4,NaHCO_3 \qquad 3NaAlSiO_4,CaSO_4.$$

These can all be prepared artificially by heating sodium aluminium silicate with a suitable salt in the presence of water under pressure. This series of compounds also includes the beautiful mineral lapis-lazuli, and artificial ultramarine, to the coloured constituent of which the name of lazurite and the formula $3NaAlSiO_4,Na_2S_3$ have been assigned. The sodalite group is also of interest as indicating the form in which salts of the more volatile acids, *e.g.*, chlorides, carbonates, and sulphates, may be retained in igneous rocks. As might be expected, they are found only in sub-silicic rocks which do not contain free quartz, and are associated with nephelite, $NaAlSiO_4$, and leucite, $KAlSi_2O_6$, usually (but not always) in eruptive rocks.

Orthosilicates.

The following types of orthosilicates may be distinguished.

(*a*) *Silicates of Quadrivalent Metals.*—**Zirconium orthosilicate,** or zircon, $ZiSiO_4$, is usually the first mineral to crystallise from a liquid magma, preceding apatite, and mica, which in its turn usually crystallises before the other silicates and quartz. It is also of interest as a member of the isomorphous series :

Zircon,	$ZrSiO_4$
Thorite,	$ThSiO_4$
Cassiterite,	SnO_2 or $SnSnO_4$
Rutile,	TiO_2 or $TiTiO_4$
Xenotime,	YPO_4,

the last being an anomalous isomorphism like that of $NaNO_3$ with $CaCO_3$.

(*b*) *Alumino-silicates.*—Many of these have the empirical formulæ of orthosilicates, containing four atoms of oxygen for each atom of silicon, *e.g.*,

(i) Nephelite, $[Na,K]AlSiO_4$, and
Anorthite, $Ca(AlSiO_4)_2$.

(ii) Micas, such as
Muscovite, $KH_2(AlSiO_4)_3$ (Fig. 196),
Phlogopite, $KH_2Mg_3AlSi_3O_{12}$ (Fig. 197),
Biotite, $KHMg_2Al_2Si_3O_{12}$.

(iii) Garnets, such as $Ca_3Al_2Si_3O_{12}$ (compare the formula of biotite, which contains $KHMg_2$ instead of Ca_3), crystallise in the cubic system, but may contain magnesium, ferrous iron, or manganese in place of calcium, and ferric iron or chromium in place of aluminium (Fig. 227, p. 623).

(c) *Silicates of Bivalent Metals.*—The most important of these is the ferromagnesian silicate OLIVINE, $[Mg,Fe]_2SiO_4$ (Fig. 198), an isomorphous mixture of **magnesium orthosilicate**, Mg_2SiO_4, and **ferrous orthosilicate**, Fe_2SiO_4. Less common minerals are also known in which manganese

FIG. 198.—OLIVINE CHANGING TO SERPENTINE. (After Geikie.)

and zinc take the place of magnesium or ferrous iron. These compounds are easily synthesised and are present in slags, but are converted into metasilicates by fusion with an excess of silica,

$$Mg_2SiO_4 + SiO_2 \rightleftharpoons 2MgSiO_3;$$

they are therefore only found in rocks which are poor in silica, *e.g.*, in basalts from which free quartz is usually absent.

Metasilicates.

(a) *Simple Metasilicates.*—**Magnesium metasilicate**, $MgSiO_3$ (p. 620), is pentamorphous. One of its five forms is only stable in the range from about 1370° to its melting-point at 1557°; of the four remaining forms, two are orthorhombic and two monosymmetric, and these four are all found in an impure state as minerals. **Calcium metasilicate**, $CaSiO_3$ (p. 640), is found in monosymmetric crystals as WOLLASTONITE, but undergoes a change of crystalline form at 1190° before melting at 1540°.

(b) *Pyroxenes and Amphiboles.*—The minerals of this group are divided into two classes, each including a less common orthorhombic and a more common monosymmetric form, namely,

(i) "Pyroxenes" cleaving into prisms with an angle of 93°, *e.g.*, AUGITE (monosymmetric), Fig. 199.

(ii) "Amphiboles" cleaving into prisms with an angle of 124°, *e.g.*, HORNBLENDE (monosymmetric).

The ferromagnesian metasilicates, AUGITE and

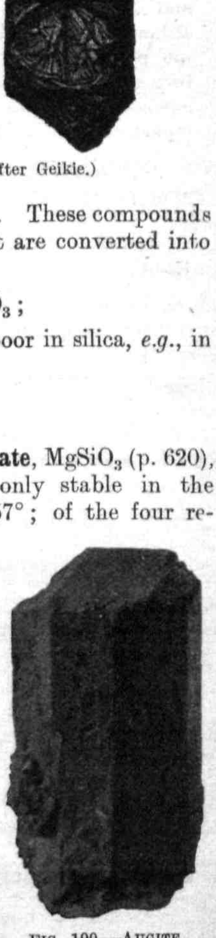


FIG. 199.—AUGITE. (British Museum, Natural History.)

Notice the vertical plane of symmetry bisecting the front of the crystal.

HORNBLENDE, [Mg,Fe]SiO_3, named above, are inferior in quantity only to the felspars and quartz.

These two minerals are both monosymmetric and are very similar in composition, since both contain ferrous oxide, magnesia, and lime as bases; in each case also the mineral may be mixed with isomorphous aluminium and ferric silicates with or without alkalies. The presence of aluminium and alkalies is attributed to an isomorphism between the alumino-silicate JADEITE, $NaAlSi_2O_6$, which also crystallises in the monosymmetric (pyroxene) system, and AUGITE, which for easier comparison may be written as $FeMgSi_2O_6$, although the Fe and Mg are not present in a constant ratio. When no alkalies are present, the aluminium is assumed to be present as an isomorphous impurity in the form of a magnesium alumino-silicate, $MgAl_2SiO_6$, which is not actually known as a mineral, the isomorphism depending on the vicarious replacement of MgSi or FeSi by Al_2.

(c) *Diopside.*—The metasilicate DIOPSIDE, $MgCa(SiO_3)_2$ (Fig. 227), is a monosymmetric pyroxene closely related to, and present as an isomorphous constituent in, AUGITE, [Mg,Fe]SiO_3. A study of the freezing-points of mixtures of the two component silicates (Fig. 200) has proved that the product is a compound, $MgCa(SiO_3)_2$, of definite composition like dolomite, $MgCa(CO_3)_2$, and not an isomorphous mixture. It is easily reproduced and has been found in devitrified bottle-glass rich in magnesia.

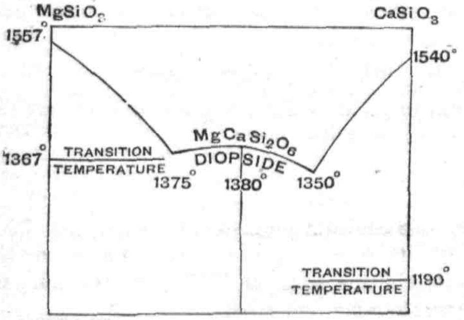


FIG. 200.—FREEZING-POINT DIAGRAM SHOWING FORMATION OF DIOPSIDE.

(d) *Complex Metasilicates.*—TALC, $H_2Mg_3(SiO_3)_4$, which is formed by eliminating one-fourth of the magnesium from magnesium metasilicate (see below), retains the formula of a metasilicate.

BERYL, $Be_3Al_2Si_6O_{18}$, a "tribasic" mineral containing 3 mols. of BeO, shows a close relationship to GARNET, $Ca_3Al_2Si_3O_{12}$, a tribasic alumino-silicate containing 3 mols. of CaO; but it contains twice as much silica and thus passes over from the class of orthosilicates into the class of metasilicates.

Decomposition of Silicates by weathering.

Attention has already been directed to the decomposition of aluminosilicates such as felspar into mica (muscovite) and quartz by eliminating two-thirds of the potassium and two-thirds of the silica, and to kaolinite and quartz by eliminating *all* the alkali and two-thirds of the silica

$$\underset{\text{Felspar}}{3KAlSi_3O_8} + CO_2 + H_2O = K_2CO_3 + \underset{\text{Muscovite}}{KH_2(AlSiO_4)_3} + 6SiO_2$$

$$\underset{\text{Felspar}}{2KAlSi_3O_8} + CO_2 + 2H_2O = K_2CO_3 + \underset{\text{Kaolinite}}{H_4Al_2Si_2O_9} + 4SiO_2$$

The ferromagnesian silicates are even more readily decomposed, giving rise to products such as SERPENTINE and TALC which also contain hydrogen and liberate water when heated. The formation of the most important of these, in which one-fourth of the magnesium is eliminated as carbonate, is shown in the following equations :

$$\underset{\text{Olivine}}{2Mg_2SiO_4} + CO_2 + 2H_2O = MgCO_3 + \underset{\text{Serpentine}}{H_4Mg_3Si_2O_9}$$

$$\underset{\text{Augite or Hornblende}}{4MgSiO_3} + CO_2 + H_2O = MgCO_3 + \underset{\text{Talc}}{H_2Mg_3Si_4O_{12}}.$$

It should be noted that whilst kaolinite is usually mixed with silica set free during its decomposition (the soluble potassium carbonate being washed away), serpentine and talc are accompanied by insoluble carbonates, *e.g.*, by marble or dolomite, but not by silica.

(*a*) SERPENTINE is a very beautiful rock formed by the decomposition of ferromagnesian orthosilicates, such as OLIVINE (Fig. 198). It is closely analogous in composition with kaolinite, from which it differs only in the replacement of Al_2 in kaolinite by Mg_3 in serpentine. By further decomposition serpentine may be converted into magnesium carbonate or sulphate and free silica. When heated, it loses water and gives a mixture of olivine or magnesium orthosilicate, Mg_2SiO_4, and enstatite, the orthorhombic pyroxene form of magnesium metal silicate, $MgSiO_3$,

$$\underset{\text{Serpentine}}{H_4Mg_3Si_2O_9} = 2H_2O + \underset{\text{Olivine}}{Mg_2SiO_4} + \underset{\text{Enstatite}}{MgSiO_3}.$$

(*b*) TALC, which is also known as a massive mineral under the name of STEATITE or SOAPSTONE, is used in a powdered form as FRENCH CHALK. Like the two preceding compounds, it is decomposed by heat, water and one-fourth of its silica being set free as shown in the equation

$$H_2Mg_3Si_4O_{12} = H_2O + 3MgSiO_3 + SiO_2.$$

Tabular Summary.

The principal mineral silicates described above may be shown in a tabular form as follows :

TABLE 58.—COMPOSITION OF MINERAL SILICATES.

A. ALUMINO-SILICATES.

(*a*) *Felspars.*

$KAlSi_3O_8$	ORTHOCLASE	(monosymmetric)	
	MICROCLINE	(anorthic)	ISOMORPHOUS.
$NaAlSi_3O_8$	ANORTHOCLASE	(,,)	ISOMORPHOUS.
	ALBITE	(,,)	ISOMORPHOUS.
$Ca(AlSiO_4)_2$	ANORTHITE	(,)	ISOMORPHOUS.

TABLE 58.—COMPOSITION OF MINERAL SILICATES (*continued*).

A. ALUMINO-SILICATES (*continued*).

(*b*) *Tribasic Compounds.*

$Ca_3Al_2(SiO_4)_3$ GARNET (cubic).
$Be_3Al_2(SiO_3)_6$ BERYL (hexagonal).

(*c*) *Micas.*—All monosymmetric and isomorphous.

$KH_2(AlSiO_4)_3$ MUSCOVITE, compare biotite and phlogopite.
$KH_2Mg_3Al(SiO_4)_3$ PHLOGOPITE, compare muscovite.
$KHMg_2Al_2(SiO_4)_3$ BIOTITE, compare garnet, $Ca_3Al_2(SiO_4)_3$.
$(AlF_2)Li_3Si_3O_8$ LEPIDOLITE, compare felspar, $NaAlSi_3O_8$.

(*d*) *Alumino-disilicates.*

$KAlSi_2O_6$ LEUCITE (cubic*).
$NaAlSi_2O_6,H_2O$ ANALCITE (,,).
$NaAlSi_2O_6$ JADEITE (monosymmetric).

(*e*) *Nephelite and Sodalite Series.*

$[Na,K]AlSiO_4$ † NEPHELITE (hexagonal).
$3NaAlSiO_4,NaHCO_3$ CANCRINITE (hexagonal).
$3NaAlSiO_4,NaCl$ SODALITE (cubic).
Also $3NaAlSiO_4,Na_2SO_4$ and $3NaAlSiO_4,CaSO_4$ (cubic).
$3NaAlSiO_4,Na_2S_3$ LAZURITE.

B. FERROMAGNESIAN SILICATES.

(*a*) *Orthosilicates.*

		Compare also :	
Mg_2SiO_4, Fe_2SiO_4	OLIVINE (orthorhombic)	$ZrSiO_4$	ZIRCON.
		$ThSiO_4$	THORITE.
$MgCaSiO_4$	MONTICELLITE (orthorhombic)	$NaAlSiO_4$	NEPHELITE.

(*b*) *Metasilicates.*

(i) *Pyroxenes* (cleavage 93°).

$[Mg,Fe]SiO_3$ ENSTATITE, etc. (orthorhombic).
$[Mg,Fe]SiO_3$‡ AUGITE (monosymmetric).
$CaSiO_3$ WOLLASTONITE (monosymmetric).
$CaMgSi_2O_6$ DIOPSIDE (monosymmetric).

(ii) *Amphiboles* (cleavage 124°).

$[Mg,Fe]SiO_3$ ANTHOPHYLLITE, etc. (orthorhombic).
$[Mg,Fe]SiO_3$‡ HORNBLENDE (monosymmetric).

* Below 433° leucite becomes doubly refracting; the external form is not altered, but the crystals consist of twin-films belonging to the orthorhombic or monosymmetric system, and are pseudo-cubic instead of cubic.

† Approximate composition.

‡ With isomorphous compounds of Ca, Al, etc.

TABLE 58.—COMPOSITION OF MINERAL SILICATES (*continued*).

C. HYDROGEN SILICATES.

(*a*) *From Alumino-silicates.*

$$\underset{\text{Felspar}}{3KAlSi_3O_8} + H_2O + CO_2 = \underset{\text{MUSCOVITE}}{KH_2(AlSiO_4)_3} + 6SiO_2 + K_2CO_3.$$

$$\underset{\text{Felspar}}{2KAlSi_3O_8} + 2H_2O + CO_2 = \underset{\text{KAOLINITE}}{H_4Al_2Si_2O_9} + 4SiO_2 + K_2CO_3.$$

(*b*) *From Ferromagnesian Silicates.*

$$\underset{\text{Olivine}}{2Mg_2SiO_4} + 2H_2O + CO_2 = \underset{\text{SERPENTINE (compare kaolinite)}}{H_4Mg_3Si_2O_9} + MgCO_3$$

$$\underset{\text{Augite or Hornblende}}{4MgSiO_3} + H_2O + CO_2 = \underset{\text{TALC}}{H_2Mg_3(SiO_3)_4} + MgCO_3.$$

Structural Formulæ of the Silicates.

(*a*) *Series of Silicates.*—A noteworthy feature of the silicates is the existence of series of compounds in which a constant amount of one or more bases is combined with an increasing proportion of silica, *e.g.*,

Nephelite, $NaAlSiO_4$
Jadeite, $NaAlSi_2O_6$
Albite, $NaAlSi_3O_8$.

They may be compared with homologous series of organic compounds (p. 448) in which increments of CH_2 are produced by inserting bivalent methylene groups in the carbon chain. In the case of the silicates the corresponding increment is SiO_2, and the tendency is to build up chains in which the bivalent group SiO alternates with bivalent atoms of oxygen, thus

$$—O·SiO·O·SiO·O—.$$

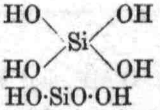
Analogous compounds have already been referred to (p. 491) in which the chain is

$$—O·SiCl_2·O·SiCl_2·O— \text{ or}$$
$$—O·SiPh_2·O·SiPh_2·O— \text{ (where } Ph = C_6H_5)$$

in contrast to the organic compounds in which the carbon atoms form a continuous chain

$$—CH_2·CH_2·CH_2—.$$

(*b*) *The silicic acids* may be formulated as follows:

Orthosilicic acid, H_4SiO_4 or 

Metasilicic acid, H_2SiO_3 or HO·SiO·OH
Disilicic acid, $H_2Si_2O_5$ or HO·SiO·O·SiO·OH
Trisilicic acid, $H_2Si_3O_7$ or HO·SiO·O·SiO·O·SiO·OH.

(*c*) ***Quartz*** is perhaps a complex silicic anhydride containing closed chains or rings of —SiO·O— groups, *e.g.*,

$$O\begin{cases} SiO\cdot O \\ SiO\cdot O \end{cases}SiO.$$

(*d*) *Aluminium silicate* and the *alumino-silicates* are most easily represented as "aluminyl" compounds containing the univalent group —AlO (compare the "antimonyl" group —SbO, p. 710), thus

Al_2SiO_5	=	$(AlO)_2SiO_3$	or	O:Al·O·SiO·O·Al:O
$NaAlSiO_4$	=	$Na(AlO)SiO_3$	or	O:Al·O·SiO·ONa
$NaAlSi_2O_6$	=	$Na(AlO)Si_2O_5$	or	O:Al·O·SiO·O·SiO·ONa
$NaAlSi_3O_8$	=	$Na(AlO)Si_3O_7$	or	O:Al·O·SiO·O·SiO·O·SiO·ONa.

They fall into line then with the very stable ferromagnesian *meta*-silicates, and also with TOPAZ (Fig. 201), $(AlF_2)AlSiO_4$, and the fluori-

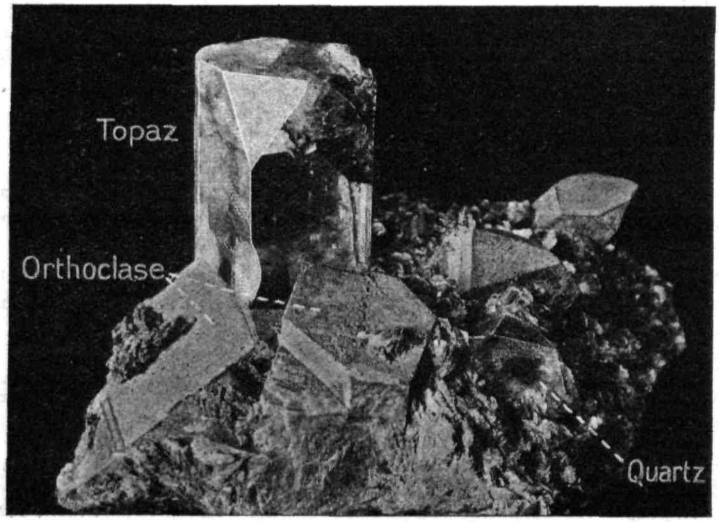


FIG. 201.—TOPAZ. With orthoclase on the left and quartz on the right. ×⅘. (British Museum, Natural History.)

ferous mica LEPIDOLITE, $(AlF_2)Li_3Si_3O_8$, in which the univalent group, $—AlF_2$, is clearly present, and which may be represented by the structural formulæ

$$OAl\cdot O\cdot SiO\cdot O\cdot AlF_2 \text{ and } F_2Al\cdot O\cdot SiO\cdot O\cdot SiO\cdot O\cdot Si(OLi)_3,$$

compare nephelite and soda-felspar,

$$OAl\cdot O\cdot SiO\cdot O\cdot Na \text{ and } OAl\cdot O\cdot SiO\cdot O\cdot SiO\cdot O\cdot SiO\cdot ONa.$$

Lime-felspar, $CaAl_2Si_2O_8$, or $Ca(AlSiO_4)_2$, the calcium salt corresponding with nephelite, $NaAlSiO_4$, may be represented as

$$\left.\begin{array}{l}O{:}Al{\cdot}O{\cdot}SiO{\cdot}O\\O{:}Al{\cdot}O{\cdot}SiO{\cdot}O\end{array}\right>Ca \quad \text{compare} \quad O{:}Al{\cdot}O{\cdot}SiO{\cdot}ONa.$$

Detection and Estimation of Silicon.

Silicon is usually detected by fusing the material with a mixture of sodium and potassium carbonates, dissolving the product in water, filtering off from the insoluble carbonates of other bases, and precipitating silicic acid by the addition of hydrochloric acid. The same process followed by ignition serves for the estimation of silica.

Silica can also be detected and estimated by the action of hydrofluoric acid upon it; the silica is then volatilised as a gaseous fluoride, SiF_4, and can in some instances be estimated directly from the loss in weight. The fluoride prepared by heating the material with fluorspar and sulphuric acid can be detected qualitatively by giving a precipitate of silicic acid in contact with water. Silicates also give insoluble particles of silica when heated in a bead of microcosmic salt.

The atomic weight of silicon has been determined by converting the chloride and bromide into oxide giving the ratios $SiCl_4 : SiO_2$ and $SiBr_4 : SiO_2$.

5. Boron. B = 11·0.

Occurrence of Boron.

Boron is a minor constituent of deep-seated igneous rocks, such as granite, where it is found as a borosilicate in the mineral TOURMALINE. This forms well-developed crystals and has been represented by the formula $3Mg(AlSiO_4)_2,B_2O_3$, compare the lime-felspar, $Ca(AlSiO_4)_2$, but on analysis it is found to be a complex isomorphous mixture like mica. The boron in this compound is volatile, the tourmaline breaking down when melted into compounds such as magnesium orthosilicate, Mg_2SiO_4, or olivine, and magnesium aluminate, or spinel, $MgAl_2O_4$. The principal sources of boron are

(i) Hot springs and "fumaroles," such as those of Tuscany, in which steam (perhaps distilled out from the igneous magma) is condensed, together with boric acid. The lagoons in which the boric acid vapours are concentrated give

Boric acid, H_3BO_3,
Ammonium borate, $(NH_4)_2B_8O_{13},4H_2O$,
Calcium borate or BOROCALCITE, $CaB_4O_7,4H_2O$, and
Ferric borate, $Fe_2B_6O_{12},3H_2O$.

The frequent association of boric acid with ammonia, especially in volcanic gases, has led to the suggestion that they may

both be derived from boron nitride, BN, a stable compound which gives these products when decomposed by steam,

$$BN + 3H_2O = H_3BO_3 + NH_3.$$

(ii) Saline residues rich in borates are also found in California, where sodium carbonate, sodium chloride, and BORAX, $Na_2B_4O_7,10H_2O$, are associated together, the boric acid being derived from hot springs near the soda-lakes.

(iii) Borates are also present in sea-water, and a series of borates of magnesium and potassium is found in the Stassfurt salt deposits.

Metallic Boron.

(*a*) *Preparation.*—Elementary boron is prepared in much the same way as silicon, *e.g.*,

(i) By the action of potassium or magnesium on potassium borofluoride,

$$3K + KBF_4 = 4KF + B.$$

(ii) By reducing the chloride with hydrogen,

$$2BCl_3 + 3H_2 = 6HCl + 2B.$$

(iii) By reducing the oxide with potassium, sodium, magnesium or aluminium, *e.g.*,

$$B_2O_3 + 2Al = Al_2O_3 + 2B.$$

On account of the greater tendency of boron to combine with metals such as aluminium (which does not form a silicide), it is necessary in all these preparations to use a large excess of boric oxide. The product is purified by extracting with hydrochloric acid, but still contains hydrides and oxides as impurities, in addition to the boride of the metal used in the reduction. These impurities can be driven off by heating the crude boron in an electric furnace in a vacuum at 1200° ; the product can then be melted down in an electric arc in an atmosphere of hydrogen.

(*b*) *Physical Properties.*—The fused product resembles crystalline or metallic silicon and shows very marked metallic conductivity. Its density is about 2·6, but its melting- and boiling-points are very high and have not yet been determined.

(*c*) *Chemical Properties.*—When heated, boron burns in air or in nitric oxide, forming boric oxide, B_2O_3, and **boron nitride**, BN, an infusible, insoluble powder, which can be prepared directly by the action of nitrogen on a mixture of boric oxide and carbon, and hydrolysed to ammonia and boric acid. Boron is not acted on by boiling water but dissolves in oxidising acids such as cold strong nitric acid, or hot sulphuric acid. Like silicon, it dissolves in potash with liberation of hydrogen,

$$2B + 2KOH + 2H_2O = 2KBO_2 + 3H_2.$$

When heated with potassium nitrate it is oxidised with explosive violence to potassium borate.

(*d*) *Metallic Borides.*—Boron forms a large number of metallic BORIDES by direct combination with the metals; these resemble the silicides both in their composition and in their properties, *e.g.*,

MnB, — , Ni_2B, NiB_2, Co_2B and CoB_2, etc.,
compare MnSi, $MnSi_2$, Ni_2Si, — , Co_2Si and $CoSi_2$, etc.

Hydrides of Boron.

These are prepared by the action of acids on crude magnesium boride prepared from magnesium and boron trioxide. The hydrides are separated from hydrogen by condensation with liquid air.

(*a*) **Borobutane**, B_4H_{10},* the principal product of this action, is a liquid with a disagreeable odour which boils at 16–17°, and freezes to a colourless solid melting at − 112°. Its vapour-density agrees with the formula B_4H_{10}. It ignites spontaneously in air or oxygen, burning with a green flame, and is oxidised explosively by concentrated nitric acid. It is decomposed by water or by dilute hydrochloric acid, and is absorbed rapidly by aqueous sodium hydroxide, liberating hydrogen as shown in the equations

$$B_4H_{10} + 12H_2O = 4H_3BO_3 + 11H_2$$
$$B_4H_{10} + 4NaOH + 4H_2O = 4NaBO_2 + 11H_2.$$

Small quantities are also obtained of a hydride, B_6H_{12}, boiling at 10° under 15 mm. pressure and at about 100° under 760 mm. pressure; it ignites spontaneously in the air and is decomposed by water and by alkalies even more readily than the preceding compound. Still smaller quantities were obtained of a hydride, $B_{10}H_{14}$, melting at 100°.

(*b*) **Boroethane**, B_2H_6.—When the hydride B_4H_{10} is kept over mercury at atmospheric temperatures, or exposed to ultra-violet light, or heated at 100° for four hours, it is decomposed, giving the hydride B_2H_6. This is a colourless gas with a repulsive odour which boils at − 88°, and freezes to a solid melting at − 169°; its density corresponds with the formula B_2H_6. It is much more stable than the hydride B_4H_{10}; thus it takes fire in the air only when other hydrides are present. It is decomposed by water quantitatively and rapidly according to the equation

$$B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2,$$

and when exploded with an excess of air is oxidised quantitatively as shown by the equation

$$2B_2H_6 + 6O_2 = 2B_2O_3 + 6H_2O.$$

(*c*) *Valency of Boron.*—It is noteworthy that the two principal hydrides of boron, B_2H_6 and B_4H_{10}, correspond in composition with

* Compare butane, C_4H_{10}.

ethane, C_2H_6, and butane, C_4H_{10}, the boiling-points being also very nearly the same, thus

B_2H_6	$-$	88°	C_2H_6	$-$	93°
B_4H_{10}	$+$	16°	C_4H_{10}	$+$	1°.

The two solid hydrides, B_6H_{12} and $B_{10}H_{14}$, which have been described also correspond in composition with known hydrocarbons, namely, hexahydrobenzene, C_6H_{12}, and hexahydronaphthalene, $C_{10}H_{14}$. There can therefore be little doubt that in these compounds boron is quadrivalent like carbon and silicon.

Boron and the Halogens.

Boron trifluoride, BF_3, can be prepared in a similar way to silicon tetrafluoride, SiF_4, by heating a mixture of boric oxide and fluorspar with sulphuric acid,

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 = 2BF_3 + 3CaSO_4 + 3H_2O.$$

It is a colourless gas (m.p. -127 °, b.p. -101°) which fumes in moist air and chars organic compounds by removing water from them. It does not attack glass directly, but parts with its fluorine to sodium and potassium, which burn brilliantly in the gas. Like silicon tetrafluoride, it combines with gaseous ammonia, forming the compounds BF_3,NH_3 (solid), $BF_3,2NH_3$ (liquid), and $BF_3,3NH_3$ (liquid), of which the first is the most stable.

When decomposed by water it gives boric acid and **borofluoric acid,** HBF_4, compare silicifluoric acid, H_2SiF_6 (p. 302):

$$4BF_3 + 3H_2O = 3HBF_4 + B(OH)_3,$$

compare $$3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4.$$

This acid gives a series of BOROFLUORIDES corresponding with the silicifluorides, *e.g.*, **sodium borofluoride**, $NaBF_4$, is formed by bringing together sodium hydrogen fluoride and boric acid,

$$2NaHF_2 + B(OH)_3 = NaBF_4 + NaOH + 2H_2O;$$

in this action two acid solutions interact to form a liquid which is strongly alkaline.

Boron trichloride, BCl_3, prepared by the action of chlorine on boron, melts at -104° and boils at 18°. Like phosphorus trichloride, it is decomposed by water, as shown in the equation

$$BCl_3 + 3H_2O = H_3BO_3 + 3HCl,$$

compare $$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

By the action of ammonia, boron trichloride is converted into **boramide,** $B(NH_2)_3$.

Boron and Oxygen.

(*a*) **Boric oxide** or **boric anhydride**, B_2O_3, prepared by igniting boric acid, melts at 577° and solidifies, like silica, to a glass.

(*b*) **Boric acid**, or SEDATIVE SALT, H_3BO_3, is prepared by adding sulphuric acid to a solution of borax in warm water,

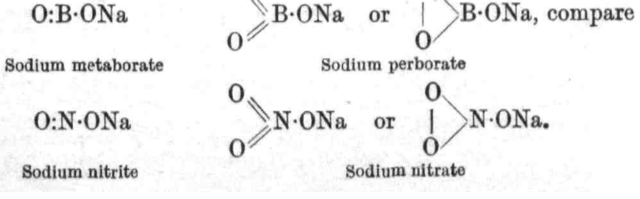
$$Na_2B_4O_7 + H_2SO_4 + 5H_2O = Na_2SO_4 + 4H_3BO_3.$$

The acid is sparingly soluble in water, a solution saturated at 0° containing 2·6 per cent. of H_3BO_3. Above 107° (when the saturated solution contains 37 per cent. of H_3BO_3) the acid separates from water as **metaboric acid**, HBO_2, whilst above about 139° a **pyroboric acid**, $H_2B_4O_7$, is obtained. When heated more strongly, the acid loses the rest of its water and is converted into boric anhydride, B_2O_3.

Boric acid is volatile in steam, which carries over 2·8 per cent. of H_3BO_3. It is a very weak acid and its sodium salt, which has an alkaline reaction, is used like soda, as a cleansing agent, under the name of borax.

(*c*) *Salts of Boric Acid.*—Although boric acid is a weak acid, its anhydride is not volatile, and will therefore displace nitric acid from sodium nitrate and sulphuric acid from sulphates. Like phosphoric and phosphorous acids, boric acid, H_3BO_3, contains 3 hydrogen atoms; but as a rule only one atom is displaced by metals in the metallic BORATES. Thus sodium orthoborate is unknown, but **sodium metaborate**, $NaBO_2,4H_2O$, can be prepared by melting together boric acid and sodium carbonate, and crystallising the product from water. The analogy between the borates and silicates is shown by the use of boric acid as a constituent of BOROSILICATE GLASS. Boric acid also shares with silicic acid the property of forming crystalline salts in which the acid is in large excess, thus, whilst sodium metaborate may be regarded as a "monoborate," Na_2O,B_2O_3, where Na : B = 1 : 1, ordinary BORAX or **sodium pyroborate,** $Na_2B_4O_7,10H_2O$, containing twice as much boron as the metaborate, is a "diborate," $Na_2O,2B_2O_3$, where Na : B = 1 : 2; the natural **calcium borates** are hydrates of a "sesquiborate," $Ca_2B_6O_{11}$, or $2CaO,3B_2O_3$; and natural **ammonium borate** is a "pentaborate" of the formula $NH_4B_5O_8,3H_2O$, or $(NH_4)_2O,5B_2O_3,6H_2O$, although an **ammonium diborate**, $(NH_4)_2B_4O_7,5H_2O$, has been prepared artificially in which NH_4 : B = 1 : 2, as in ordinary borax.

(*d*) *Perborates.*—By the action of hydrogen peroxide on a borate, or by electrolytic oxidation of the borate of an alkali, PERBORATES have been prepared, which decolorise potassium permanganate and liberate iodine from potassium iodide. **Sodium perborate,** $NaBO_3,4H_2O$, is a commercial product and may be represented as the analogue of sodium nitrate, $NaNO_3$:



It is used extensively as a mild bleaching agent for laundry-work. The sodium salt of a **per*tetra*boric acid**, $Na_2B_4O_{11}$, has also been prepared.

Boron and Sulphur.

Boric sulphide, B_2S_3, is prepared by direct combination of boron with sulphur or by heating boron in a current of sulphuretted hydrogen. It sublimes in white needles, melts at 310° and is decomposed violently by water,

$$B_2S_3 + 6H_2O = 2H_3BO_3 + 3H_2S.$$

It combines with ammonia to form a compound, $B_2S_3,6NH_3$, which on gentle heating gives **borimide**, $B_2(NH)_3$, and on stronger heating leaves a residue of the nitride,

$$B_2N_3H_3 = 2BN + NH_3.$$

A **diboron pentasulphide**, B_2S_5, is also known.

Detection and Estimation of Boron.

Metallic borates are usually insoluble in water, but soluble borates give a white precipitate of **silver borate** when silver nitrate is added, and from strong solutions **boric acid,** H_3BO_3, can be precipitated by the addition of an acid. Boric acid is also characterised by giving with turmeric a brown colour which becomes bluish-black on the addition of alkali. Boric acid (or a borate), when heated with methyl alcohol and sulphuric acid, forms **methyl borate,** $B(OCH_3)_3$, compare $B(OH)_3$, a liquid which boils at 65° and burns with a green flame; the formation of this volatile compound is used as a qualitative test for boric acid, and also in the quantitative estimation of the acid by distilling the methyl borate into lime and weighing the B_2O_3 which it retains. Boric acid can be titrated by taking advantage of the fact that, whilst a weak acid itself, it forms a strong monobasic acid by combination with glycerine, $C_3H_5(OH)_3$, or with mannitol, $C_6H_8(OH)_6$; the solution is made neutral to methyl-orange, and glycerine or mannitol is added, when an acid reaction is developed; the solution is then titrated until neutral to phenolphthalein.

The atomic weight of boron has been determined from the dehydration of borax, $Na_2B_4O_7,10H_2O$, but this method is not satisfactory. It has also been deduced from the ratios $Na_2B_4O_7 : 2NaCl$, $BCl_3 : 3AgCl$ and $BBr_3 : 3AgBr$.

INORGANIC CHEMISTRY

PART III.—THE METALS: TYPICAL SERIES

CHAPTER XXX

GENERAL PROPERTIES OF THE METALS

Metals and Non-metals.

The simplest classification of the elements is into two groups, as METALS and NON-METALS. This classification depends on the well-known physical properties of the elements. Thus, metals such as iron, copper, and zinc can easily be distinguished by their totally different physical properties from non-metals such as oxygen, chlorine, and sulphur. The typical metal is an opaque, lustrous, heavy solid, usually possessing valuable mechanical properties. A typical non-metal, on the other hand, may be a gas, such as hydrogen, oxygen, nitrogen, or chlorine, a liquid such as bromine, or a solid such as phosphorus, sulphur, or iodine; but it is generally transparent, of low density, and devoid of strength, ductility, malleability, and other similar mechanical properties.

Physical Properties of the Metals.

Unfortunately, these physical properties cannot be used as the basis of a precise definition of metals and non-metals.

(*a*) *Density*.—The heaviest elements are all metals, *e.g.*,

	Density.		*Density.*
Iridium	22·4	Gold	19·3
Platinum	21·4	Tungsten	19·1

but other elements which are certainly metallic do not possess the property of high density, *e.g.*,

	Density.		*Density.*
Aluminium	2·7	Sodium	0·97
Beryllium	1·8	Potassium	0·86
Magnesium	1·7	Lithium	0·53

and one of these, namely lithium, is one of the lightest known solids. Between these two extreme groups the following metals are found :

	Density.		Density.
Mercury	13·6	Nickel, Cobalt	8·8
Lead	11·3	Iron	7·8
Silver	10·5	Tin	7·3
Copper	8·9	Zinc	7·1

(*b*) *Melting-point.*—Again nearly all the metals are solids, and many of them can only be melted at a very high temperature, as, for instance,

	Melting-point.		Melting-point.
Tungsten	about 3060°	Iridium	about 2350°
Tantalum	about 2900°	Platinum	1755°

but other metals are very easily melted, and mercury is liquid at the ordinary temperature, thus,

	Melting-point.		Melting-point.
Sodium	+ 97·5°	Gallium	+ 30·1°
Potassium	+ 62·5°	Cæsium	+ 28·2°
Rubidium	+ 38·5°	Mercury	− 39·0°

Between these two groups the following metals are found :

	Melting-point.		Melting-point.
Chromium	1615°	Aluminium	659°
Iron	1530°	Magnesium	650°
Cobalt	1480°	Antimony	630°
Nickel	1452°	Zinc	419°
Manganese	1230°	Lead	327°
Copper	1083°	Cadmium	321°
Gold	1062°	Bismuth	271°
Silver	960°	Tin	232°.

Mixtures of metals are even more fusible than the metals themselves and are therefore used extensively for the manufacture of solders and fusible alloys, *e.g.*,

	Per cent.		Per cent.	Melting-point.
Pb	36	Sn	64	+ 181°
Pb	25	Sn	14	+ 66°
Bi	50	Cd	11	
K	77	Na	23	− 12·5°

(*c*) *Mechanical Properties.*—The valuable mechanical property of TENACITY or TENSILE STRENGTH, combined either with HARDNESS or with DUCTILITY and MALLEABILITY, which have made the metals the basis of modern civilisation, are also by no means universally displayed by the metals, some of which are either brittle or excessively soft,

whilst others cannot be used on account of the ease with which they become corroded.

Metallic Lustre and Metallic Conductivity.

In seeking for an exact definition of a metal, two properties stand out as being particularly suitable for this purpose, namely, METALLIC LUSTRE and METALLIC CONDUCTIVITY. These two properties are so far characteristic of the metals that they are commonly described by the adjective "metallic."

(*a*) *Metallic lustre* depends on two physical qualities, namely, great opacity and ability to take a high polish. Certain compounds of the metals (see below, p. 527) possess it, but amongst the elements there are very few non-metals in which anything resembling metallic lustre is seen. Thus, the lustre of crystals of iodine is almost metallic, but not fully so, since the material is not completely opaque. Carbon in the form of GRAPHITE, which is often used under the name of BLACK LEAD to impart a metallic polish to iron fireplaces, and crystalline or METALLIC SILICON, possess this property in a more marked degree.

(*b*) *Metallic conductivity* is the property of carrying an electric current without being decomposed thereby. This property is confined almost exclusively to the metals, as is shown in the following table of specific conductivities:

TABLE 59.—SPECIFIC CONDUCTIVITY OF METALS.

Metal.	*Temperature.*	*Conductivity.* Reciprocal ohms per cm. cube.		*Relative values.* Copper = 100
Silver	0°	67 × 10^4		105
Copper	0	64 ,,		100
Aluminium	0	39 ,,		61
Lead	0	5 ,,		7·8
Arsenic	0	2·8 ,,		4·5
Antimony	0	2·6 ,,		4·1
Silicon	—	1·7 ,,		2·7
Mercury	0	1·063 ,,		1·7
Bismuth	0	0·92 ,,		1·4
Graphite	0	0·09 ,,	or 900·0 units	0·15
Galena, PbS	20		377 ,,	0·05
Iron pyrites, FeS_2	20		42 ,,	0·005
Magnetite, Fe_3O_4	17		1·68 ,,	0·0002

Apart from silicon and graphite, none of the elements commonly classed as non-metals possesses any appreciable metallic conductivity; indeed the modern theory of light suggests that this form of conductivity can only appear in opaque substances, so that carbon in the form of diamond is necessarily an insulator. The three minerals, galena, pyrites, and magnetite, which are included in the table as showing a slight metallic conductivity, are also all opaque and possess a marked metallic lustre. In the case of graphite, the combination of metallic lustre and metallic

conductivity is so striking as to lend strong support to the view that graphite should be regarded as a metallic form of carbon, whilst diamond is a non-metallic form of the same element.

Mechanical Properties of the Metals.

(*a*) *Plasticity.*—The metals are unique in combining great strength with a high degree of PLASTICITY. Whereas a viscous substance (p. 3) will undergo permanent deformation under the influence of very small forces, *e.g.*, under gravity (compare pitch, Fig. 2), a plastic substance will only do so when acted upon by forces greater than a fixed minimum value. This minimum value is called the ELASTIC LIMIT of the material.

In the case of metals, the elastic limit is generally measured, like the tensile strength, in tons per square inch, *e.g.*, for mild steel the figures are approximately :

Elastic limit,	14 tons per square inch.
Tensile strength,	20 ,, ,, ,, ,,

When the elastic limit is exceeded the material begins to stretch and finally breaks. The TOUGHNESS of a metal is indicated (i) by the margin between

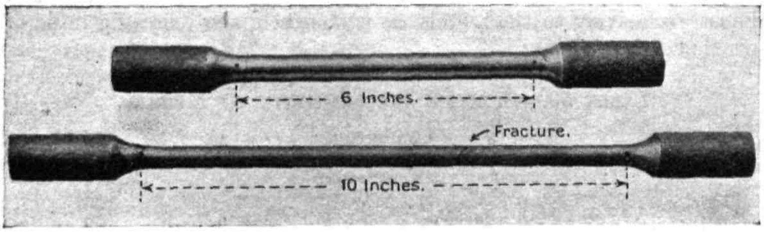


FIG. 202.—TEST-PIECES OF MANGANESE STEEL.

the elastic limit at which it begins to stretch and its tensile strength or "ultimate strength," as measured by the force required to break it ; (ii) by the *elongation* which the test-piece undergoes before it breaks ; (iii) by the *reduction of area* of a section of the test-piece, as well as (iv) by bending and twisting tests. A typical test-piece of manganese steel is shown in Fig. 202. This gave an elongation of 3·84 inches on a length of 6 inches, or 64 per cent. ; a reduction of area from 0·259 to 0·142 square inch, or 45·2 per cent. ; and a tensile strength of 72·3 tons per square inch. This combination of great ductility with high tensile strength is, however, exceptional.

(*b*) *The Working of Metals.*—The plasticity of pure metals and of some alloys is made use of in drawing DUCTILE METALS into wire, hammering MALLEABLE METALS into leaf or foil, or rolling them into sheets or plates, and finally in squirting or "extruding" the softer metals by forcing them through a die. Thus pure gold can be hammered out into GOLD LEAF 0·0001 mm. in thickness, or drawn out into wire 0·005 mm. (0·0002 inch) in diameter. Even on a commercial scale copper wire can be drawn out to 0·0015 inch (1·5 mil or about

0·04 mm.) or at greater cost to 0·001 inch (1 mil or 0·026 mm.), and tungsten filaments to 0·0014 inch (1·4 mil).

Silver, copper, platinum, iron, nickel, aluminium, zinc, and lead are used extensively as sheet-metals, whilst lead, tin, silver, and aluminium are used as foil. Platinum, silver, copper, iron, and aluminium are used as wire. Lead can be extruded by pressure into rods or pipes, and sodium can be pressed through a die in the form of wire. A few metallic alloys are sufficiently plastic to be worked in the same way as the pure metals, *e.g.*, brass can be rolled into sheets and drawn into wire when cold, or extruded from a die when hot, and steel can be rolled into plates or into thin sheets (for galvanising and tinning) at a red heat. Wrought iron, which is the purest form of commercial iron, is plastic enough to be welded at a red heat, just as gold and pure clean lead can be welded into a homogeneous mass at atmospheric temperatures.

(*c*) *The Crystalline and Amorphous States of Metals.*—The plasticity of a metal is related closely to its crystalline character, and depends largely on the readiness with which the layers of atoms of which the crystals are composed can be made to slide over one another, giving rise to GLIDING PLANES, which are seen in section as SLIP-BANDS when a polished surface of the metal is examined under the microscope. This sliding, if repeated, results in considerable disturbance to the regular marshalling of the atoms, and thus produces a film of amorphous or glassy material, which no longer possesses the regular structure or the plasticity of the original crystals. A metal is therefore usually hardened by working, but can be softened again by ANNEALING, *i.e.*, by heating it to the temperature at which the glassy metal can crystallise again. Lead and tin, however, cannot be hardened permanently by deformation, since they anneal themselves at atmospheric temperatures and cannot therefore be retained in the glassy or amorphous condition.

(*d*) *Alloys.*—The mechanical properties of a metal may be modified profoundly by alloying it with another element, *e.g.*, by melting the two elements together and allowing the liquid to crystallise. In accordance with the general rule that " like dissolves like," molten metals will often mix with one another in all proportions. Zinc, however, gives two layers when mixed with lead below 935° or with bismuth below 820°, whilst aluminium gives two layers with lead, with bismuth, and with cadmium ; altogether about 40 cases of partial miscibility of metals have been described.

In general, the readily fusible metals, Pb, Cd, Bi, Sn (p. 684), do not mix freely with the transition-metals (p. 719), Cr, Mn, Fe, Co, Ni, Cu, Zn. Thus :

{ *Lead* is not miscible with Al, Si ; Cr, Mn, Fe, Co, Ni, Cu, Zn.
{ *Bismuth* is not miscible with Al, Si, As ; Cr, Fe, Co, Zn.
{ *Silver* (resembling lead) is not miscible with Cr, Mn, Fe, Co, Ni.

{ *Chromium* is not miscible with Pb, Cd, Bi, Sn, nor with Cu or Zn.
{ *Aluminium* (resembling chromium) is not miscible with Pb, Cd, Bi, Tl, Na, K, nor with Mn.

In addition to the metals, some non-metals, including oxgyen, sulphur, phosphorus, carbon, and silicon, will dissolve in molten metals, probably in the form of quasi-metallic compounds (p. 527), and may therefore appear either as valuable constituents in an alloy or as deleterious impurities in a simple metal or in an alloy.

(*e*) *Structure of Alloys*.—It has already been shown (p. 180) that when a binary alloy crystallises the two constituents may (i) separate more or less completely, giving rise under suitable conditions to an "eutectic alloy"; (ii) remain in solid solution after crystallisation; (iii) form one or more chemical compounds with one another.

Metals which are very similar or very closely related usually form a complete series of solid solutions with one another, *e.g.*,

silver and *gold*, *gold* and *platinum* (Fig. 67, p. 181),
iron and *nickel*, *nickel* and *cobalt* (Fig. 265, p. 776).

Where the two metals resemble one another, but are not identical in crystalline form, two (or more) series of solid solutions may be formed, one having the form of the first metal and another the form of the second metal, *e.g.*,

cadmium and *mercury* (Fig. 68, p. 182).

The first sign of incompatibility between two metals is, however, often seen in a drooping freezing-point curve, *e.g.*,

nickel and *manganese*, *manganese* and *copper* (Fig. 256, p. 754).

Those metals which are less closely related often form eutectic alloys, *e.g.*,

tin and *lead* (Fig. 69, p. 182), *lead* and *silver*, *silver* and *silicon*.

Finally, when there is a marked contrast between the two metals, definite INTERMETALLIC COMPOUNDS may be formed (p. 185); these resemble the metals in appearance and in many of their properties and can be represented by definite chemical formulæ, but they appear to be entirely independent of the ordinary rules of valency, as is shown in the following series of compounds:

Gold and *aluminium*, Au_4Al, Au_2Al, $AuAl_2$, etc.
Sodium and *mercury*, $NaHg_4$, $NaHg_2$, NaHg, etc.
Potassium and *mercury*, KHg_2, KHg, etc.

(*f*) *Mechanical Properties of Alloys*.—When two metals separate completely from one another on crystallisation, the alloy usually consists of thin bands of the two constituents, often enclosing larger crystals of one of them (Figs. 70 and 71, pp. 183 and 184). Its properties should then not differ very widely from those which would be predicted for a composite structure of this kind. But in all other cases the mechanical properties of the alloy may be modified profoundly by the mutual dissolution or chemical combination of the two constituents.

When solid solutions are formed it might perhaps have been expected that the mechanical properties of the alloy would be approximately the mean of those of its constituents, as in the case of the density, freezing-point, and optical properties of many isomorphous mixtures; but this is not so, since it is found that a solid solution of two metals is almost always harder and of greater ELASTICITY (*i.e.*, requires a greater stress to produce a given strain) than the constituent metals. This

rigidity of the solid solution is perhaps due to the fact that although the crystal-structure is similar to that of the pure metals, it is not quite so easy to cause the layers of atoms to slip over one another as when only one kind of atom is present.

When chemical compounds are formed, the contrast of properties is still more marked. In particular, it is remarkable that no chemical compound is known which possesses the toughness (strength and plasticity) of a pure metal. Metallic compounds, on the contrary, are nearly always characterised by great BRITTLENESS (*i.e.*, they are not capable of undergoing any large deformation without fracture) although they may be very hard and very strong to resist both crushing and tensile stresses.

(*g*) *Classification of Alloys*.—The most important series of alloys are derived from the three metals

aluminium, *copper*, and *iron*.

In the pure state all these metals are soft and plastic, lending themselves readily to the manufacture of sheet, foil, or wire. This softness also enables them to take up considerable proportions of other elements in *solid solution* without being rendered unduly brittle thereby; they therefore give rise to a very wide range of useful alloys, including the light alloys of aluminium (p. 655), the brasses (copper and zinc, p. 833) and bronzes (copper and tin, p. 834), as well as the important group of steels (p. 774).

Where hardness rather than toughness is required, alloys containing *chemical compounds* are frequently used; great hardness can, however, also be produced (as in quenched steel, p. 771) by making use of a solid solution in the state of strain caused by the incipient crystallisation of its constituents, where these tend to separate from one another as the temperature falls. The alloys used as bearing-metal for the bearings of shafts are selected so as to contain a hard compound in a matrix of a soft metal. Finally, attention may be directed to the use of *eutectic alloys* of metals of low melting point, lead, tin, bismuth, cadmium, etc., for solders and fusible alloys (p. 684), where ease of melting is more important than strength or toughness, and to the special metals and alloys which are selected to meet various chemical requirements, *e.g.*, platinum, tungsten, aluminium, stainless steel, acid-resisting alloys, etc.

Quasi-metallic Compounds and their Alloys.

Attention has already been directed (p. 523) to the fact that certain minerals, including iron pyrites, FeS_2, galena, PbS, and magnetite, Fe_3O_4, possess both metallic lustre and some degree of metallic conductivity. These minerals may be regarded as typical of a group of QUASI-METALLIC COMPOUNDS which have acquired considerable technical importance in view of the fact that they will dissolve in molten metals

and in some cases will also form solid solutions with metals in the crystalline state, thus exerting a profound influence on the metals with which they are alloyed. These quasi-metallic compounds include

oxides,	such as Cu_2O,
sulphides,	such as FeS, NiS, and Cu_2S,
phosphides,	such as Fe_3P and Cu_3P,
arsenides,	such as FeAs, NiAs and Cu_3As,
carbides,	such as Mn_3C and Fe_3C,
silicides,	such as Fe_2Si, FeSi, etc. (p. 487).

In almost every case these compounds form eutectic alloys with the metal which they contain, or with some compound of intermediate composition.

The metallic constituent is always a heavy metal, since the compounds of the alkalies and alkaline earths, as well as of the lighter metals, are usually more salt-like in their character, *e.g.*, sodium and calcium sulphides are colourless and soluble in water, and even zinc sulphide is colourless when pure and forms transparent instead of opaque crystals.

The metallic sulphides are of special interest in view of the important part played in metallurgy by their alloys with one another, as well as with the metals ; in particular, the metallurgy of copper, nickel, and antimony depends on the manipulation of fused mixtures of sulphides, to which the name of MATTE is generally given, and which correspond in many respects with the metallic alloys. The corresponding mixtures of arsenides are described as SPIESS.

Chemical Properties of the Metals.

Lavoisier classified the elements into three principal groups, namely,

(i) *Metals*, which could be oxidised and converted into bases,
(ii) *Non-metals*, which could be oxidised and converted into acids,
(iii) *Oxygen*, which occupied a unique position as the element by which metals were converted into bases and non-metals into acids.

The earths such as lime were provisionally classified in a fourth group, although Lavoisier already suspected that they might be metallic oxides.

In this scheme, salts were regarded as oxygen-compounds, formed by the union of the basic oxide of a metal with the acid oxide of a non-metal. This classification was followed by Davy, who was obliged, however, to include chlorine with oxygen as one of the group of elements which could support combustion. The vapours of sulphur and phosphorus can also act under some conditions as supporters of combustion. The unique position assigned by Lavoisier to oxygen, and by Davy to oxygen and chlorine, has therefore not been maintained

in later classifications, which have invariably included oxygen and chlorine with sulphur and phosphorus, in the general group of non-metals.

Attempts have frequently been made to distinguish metals from non-metals by means of their chemical properties, but it is very difficult to make these properties the basis of an exact definition. Thus, if it be argued that an element which gives basic oxides is a metal, whilst an element which gives acid oxides is a non-metal, it is necessary to recognise :

(i) That some elements form both acid and basic oxides, as, for instance :

Chromium.			*Manganese.*
Chromous oxide,	CrO,	base	Manganous oxide, MnO, basic
Chromic oxide,	Cr_2O_3,	weak base	Manganese dioxide, MnO_2, doubtful
Chromic anhydride,	CrO_3,	acid	Manganese trioxide, MnO_3, acid
			Dimanganese heptoxide, Mn_2O_7, acid.

(ii) That when only a single oxide is produced, this may possess both acid and basic properties ; such oxides are described as AMPHOTERIC OXIDES (Greek, ἀμφότερος, both) and include the oxides of zinc and of aluminium, which are capable of forming salts both with strong acids and with strong bases, thus,

$$\underset{}{ZnO} + 2HCl = \underset{\text{Zinc chloride}}{ZnCl_2} + H_2O$$

$$ZnO + 2NaOH = \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2O$$

$$Al_2O_3 + 6HCl = \underset{\text{Aluminium chloride}}{2AlCl_3} + 3H_2O$$

$$Al_2O_3 + 2NaOH = \underset{\text{Sodium aluminate}}{2NaAlO_2} + H_2O$$

Similar difficulties are encountered when attempts are made to classify the elements according to the properties of their chlorides. Thus, if common salt or sodium chloride, $NaCl$, be taken as a typical metallic chloride, and carbon tetrachloride, CCl_4, as a typical non-metallic chloride, it is found that tin forms one chloride of each type, stannous chloride, $SnCl_2$, agreeing generally with the properties of the metallic chlorides, whilst stannic chloride, $SnCl_4$, is an oil resembling carbon tetrachloride, although it differs from it in being soluble in water.

It appears therefore that whilst a general description may be given of the chemical properties of the metals, as usually forming basic oxides and so forth, these properties cannot be made the basis of an exact definition of the two groups of elements. If, however, the

adjectives metallic and non-metallic be regarded as descriptive of the physical properties of an element rather than of its chemical properties, the classification is easier, and there does not appear to be any reason why, in the case of an element such as carbon, the existence of a metallic and a non-metallic form of the same element should not be admitted. As regards the differences of atomic and molecular structure which give rise to these two types of physical properties, little is at present known.

CHAPTER XXXI

THE CLASSIFICATION OF THE ELEMENTS

Triads.

Döbereiner in 1829 directed attention to the fact that the atomic weight and properties of *bromine* are very near the average of those of *chlorine* and *iodine*, whilst those of *selenium* approximate to the average of those of *sulphur* and *tellurium*. Thus, taking the modern values for the atomic weights, we have in round numbers :

Cl = $35\frac{1}{2}$	Br = 80	I = 127.	Mean of Cl and I = 81.
S = 32	Se = 79	Te = $127\frac{1}{2}$.	Mean of S and Te = 80.

In the case of the metals, similar relationships were detected in the groups

Li = 7	Na = 23	K = 39.	Mean of Li and K = 23
Ca = 40	Sr = 88	Ba = 137.	Mean of Ca and Ba = $88\frac{1}{2}$,

as well as in certain groups where the atomic weights differ but little as in

Ni = 59	Cu = 63	Zn = 65.	Mean of Ni and Zn = 62
Os = 191	Ir = 193	Pt = 195.	Mean of Os and Pt = 193.

These groups of three elements, with atomic weights in arithmetical progression, became known as TRIADS.

As an illustration of the properties of a triad, the data for the halogens are given in Table 60, from which it will be seen that the properties of bromine are very near the average of those of chlorine and iodine, but a little nearer to iodine than to chlorine.

TABLE 60.—PROPERTIES OF THE HALOGENS.

	Atomic weight.	*Melting-point.*	*Boiling-point.*	*Density.*
F	19·0	− 233°	− 187°	1·14 at − 200°
Cl	35·46	− 102°	− 33·7°	1·42 at 18°
Br	79·92	− 7·3°	+ 58·6°	3·14 at 18°
I	126·92	+ 113°	+ 184°	4·94 at 17°
$\frac{Cl + I}{2}$	81·19	+ 5·5°	+ 75°	3·18

TABLE 60.—PROPERTIES OF THE HALOGENS (*continued*).

	Melting-point.	*Boiling-point.*	*Heat of Formation* Gaseous.	*Heat of Formation* Dissolved.
HF	− 92°	+ 19·5°	+ 38,500 cal.	+ 50,300 cal.
HCl	− 111°	− 83°	+ 22,000 cal.	+ 39,400 cal.
HBr	− 86°	− 69°	+ 8,600 cal.	+ 28,600 cal.
HI	− 51°	− 36°	− 6,400 cal.	+ 13,200 cal.
$\frac{HCl+HI}{2}$	− 81°	− 59·5°	+ 7,800 cal.	+ 26,300 cal.

Natural Series or Families of Elements.

Dumas in 1859 converted these triads into families or NATURAL SERIES OF elements by including fluorine with chlorine, bromine, and iodine, and oxygen with sulphur, selenium, and tellurium, etc. He also showed that some of these series of elements resembled one another in that the differences between successive elements were sometimes the same, the atomic weights of one series being consistently four or five units higher than those of another series, thus

Nitrogen family.		*Fluorine family.*		*Difference.*
N = 14		F = 19		F − N = 5
	+ 17		+ 16½	
P = 31		Cl = 35½		Cl − P = 4½
	+ 44		+ 44½	
As = 75		Br = 80		Br − As = 5
	+ 47		+ 47	
Sb = 120		I = 127		I − Sb = 7

Dumas also directed attention to the analogy between these series of elements and the homologous series of organic compounds (p. 448), which differ from one another by increments of $CH_2 = 16$; this conception still survives in the usage whereby chlorine, bromine, and iodine are commonly described as the " homologues " of fluorine, and so forth. Dumas's " natural series," and the relationships which he discovered between them, found a full expression shortly afterwards in the periodic classification of the elements, which came to light almost immediately after the atomic weights had been worked out upon a correct basis by Cannizzaro and others.

Periodic Classification of the Elements.

(*a*) *Newlands's Octaves.*—It was discovered by Newlands in 1864 that, if the elements were arranged in the order of their recently established atomic weights, the elements of Dumas's natural series or families were distributed at regular intervals like octaves in music, *i.e.*, the members of a series were separated from one another by six elements belonging to other series and possessing widely different pro-

perties; similar properties appeared only when the eighth element or octave was reached. Newlands's OCTAVES can still be recognised in the Periodic Classification of the Elements (Table 61, p. 534), where the principal families of elements are found in the vertical columns headed I to VII, *e.g.*, the metals of the alkalies in column I, and the family of halogens in column VII.

(*b*) *Mendeléeff's Short and Long Periods.*—Newlands's list of elements was already too extensive to be confined within the limits of his octaves, and in certain cases he was obliged to crowd two elements into a single space in the table, in order to maintain the others in their proper positions as members of natural families of elements. In order to overcome this difficulty, Mendeléeff in 1869 introduced an additional column VIII (Table 61), in which he placed triads of elements following the alternate octaves of Newlands's table. The elements after hydrogen were thus grouped into two SHORT PERIODS or octaves of seven elements followed by four LONG PERIODS each containing two octaves and a triad or

$$7 + 3 + 7 = 17 \text{ elements.}$$

The outlines of this classification can again be recognised in Table 61.

(*c*) *Odd and Even Series.*—The natural families of elements, such as the alkali-metals and the halogens, are distributed equally in the short and long periods, one element in each period, whether short or long. There is therefore a marked contrast between the two octaves of each long period, since one octave contains an alkali-metal and no halogen, whilst the other octave contains a halogen but no alkali-metal. Mendeléeff sought to express this contrast by distinguishing the alternate octaves as ODD and EVEN SERIES. This scheme is, however, unsatisfactory, since the alkali-metals are found at the beginning of the octaves 1, 2, 3, 5, 7, and the halogens at the ends of the octaves 1, 2, 4, 6, but in neither case is this a complete odd or even series. A far more satisfactory method of discrimination therefore is to group into families the analogous elements which are found at the beginning of each period, whether short or long, *e.g.*, the metals of the alkalies and of the alkaline earths, and the analogous elements at the end of each period, *e.g.*, the halogens, and to consider the elements occupying the centres of the long periods separately as TRANSITION-ELEMENTS (see Chapter XXXVII), linking together the earlier and later elements of the period.

(*d*) *Modern Classification of the Elements.*—A modern form of the periodic classification of the elements is shown in Table 61. The elements are here grouped in seven periods as follows:

Period I . .	1 element	
Period II . .	8 elements	Short periods.
Period III . .	8 elements	

TABLE 61.—ATOMIC NUMBERS AND ATOMIC WEIGHTS.

	0	I	II	III	IV	V	VI	VII	VIII		
PERIOD I. (1 Element)								1 H 1·008			
„ II. (8 Elements)	2 He 4·00	3 Li 6·94	4 Be 9·1	5 **B** 10·9	6 **C** 12·005	7 **N** 14·008	8 **O** 16	9 **F** 19·0			
„ III. (8 Elements)	10 Ne 20·2	11 Na 23·00	12 Mg 24·32	13 Al 27·1	14 **Si** 28·3	15 **P** 31·04	16 **S** 32·06	17 **Cl** 35·46			
„ IV. (18 Elements)	18 A 39·9	19 K 39·10	20 Ca 40·07	21 Sc 45·1	22 Ti 48·1	23 V 51·0	24 Cr 52·0	25 Mn 54·93	26 Fe 55·84	27 Co 58·97	28 Ni 58·68
		29 Cu 63·57	30 Zn 65·37	31 Ga 70·1	32 Ge 72·5	33 **As** 74·96	34 **Se** 79·2	35 **Br** 79·92			
„ V. (18 Elements)	36 Kr 82·92	37 Rb 85·45	38 Sr 87·63	39 Yt 89·33	40 Zr 90·6	41 Cb 93·1	42 Mo 96·0	43 ? —	44 Ru 101·7	45 Rh 102·9	46 Pd 106·7
		47 Ag 107·88	48 Cd 112·40	49 In 114·8	50 Sn 118·7	51 Sb 120·2	52 **Te** 127·5	53 **I** 126·92			
„ VI. (32 Elements)	54 Xe 130·2	55 Cs 132·81	56 Ba 137·37	57–71 RARE EARTHS	72 ? —	73 Ta 181·5	74 W 184·0	75 ? —	76 Os 190·9	77 Ir 193·1	78 Pt 195·2
		79 Au 197·2	80 Hg 200·6	81 Tl 204·0	82 Pb 207·20	83 Bi 208·0	84 ? —	85 ? —			
„ VII. (? Elements)	86 Nt 222·4	87 ? —	88 Ra 226·0	89 ? —	90 Th 232·15	91 ? —	92 U 238·2				

Period IV . .	18 elements	Long periods.
Period V . .	18 elements	
Period VI . .	32 elements	Very long periods (?).
Period VII . .	4 + ?	

The number of columns in the table, which was increased from seven to eight by Mendeléeff, has been increased still further by the addition of a column 0 to contain the inert gases of the helium family. The number of periods, on the other hand, has been diminished by clustering together in a single space of the table the 14 or 15 elements of the "rare earths" (p. 666), and thus compressing two of Mendeléeff's long periods of 17 or 18 elements into a single "very long period" of 32 elements. Under these conditions the rule that one element of each family should be found in each period can be vindicated in the case of all the more complete families: thus each of the periods II to VI begins with a gas of the helium type, followed by an alkali metal (with the exception of period VII, where it is missing) and then by an element of the group of alkaline earths.

It may be noted that the 14 elements in heavy type, occupying the ends of the short and long periods and forming a rough triangle in the table, include all the important non-metals, the hypotenuse (which forms the main boundary of the triangle) being occupied by four elements, B, Si, As, Te, which have the physical properties of metals, but resemble the non-metals in their chemical properties (acidic oxides, etc.). The gases of the helium group would also form a side of this triangle if transferred from the beginning of periods II to VII to the end of periods I to VI; this arrangement would be equally correct, but much less convenient, since it would bring two types of elements into column VIII, thus reproducing in an extreme form the contrast which led Mendeléeff to discriminate between odd and even series of elements.

Atomic Numbers.

In Table 61 the elements are indicated by serial numbers from 1. Hydrogen, to 92. Uranium. These ATOMIC NUMBERS have a definite experimental basis, depending on a regular progression which has been discovered in the frequency of the radiation given out when the different elements are used as the anti-cathode (p. 541) of an *X*-ray tube. Thus, the square root of the frequency of the principal rays increases by equal increments in the series

Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn,

when these elements or their compounds are used as the anti-cathode in the tube (Figs. 203 and 204). By this method it has been established that if the atomic number 13 be assigned arbitrarily to aluminium, then the serial number of gold is 79.

(*a*) *Atomic Numbers and Atomic Weights.*—The experimental

determination of the atomic numbers has an important bearing on the fact that, in order to maintain a proper classification of the elements, it

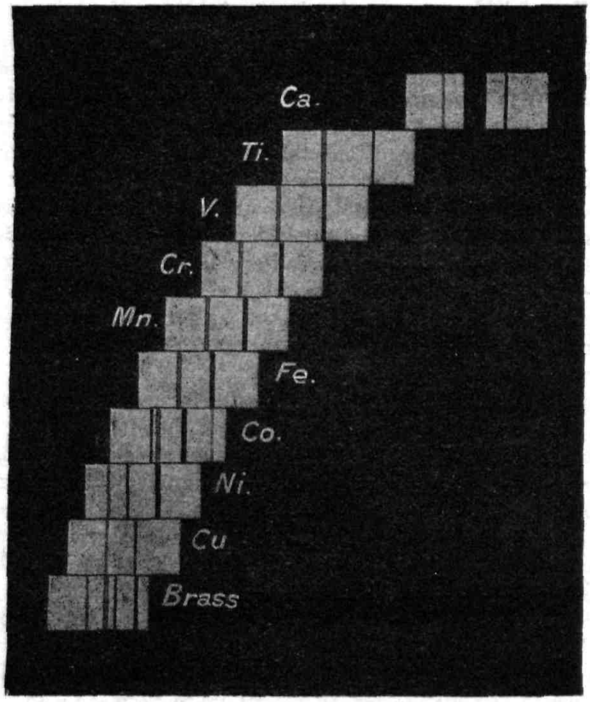


FIG. 203.—*X*-RAY SPECTRA OF THE ELEMENTS FROM CALCIUM TO ZINC (Moseley).

The spectrum of each element consists of two principal lines, but the cobalt-spectrum shows lines due to the presence of iron and nickel, the nickel appears to have contained some copper and the brass gives two lines due to copper and two lines due to zinc.

has been necessary in three cases to arrange pairs of elements in the inverse order of their atomic weights as follows:

Atomic number	*Element.*	*Atomic weight.*
18	Argon	39·88
19	Potassium	39·10
27	Cobalt	58·97
28	Nickel	58·68
52	Tellurium	127·5
53	Iodine	126·92

This inversion (as may be seen by referring to Figs. 203 and 204) is justified by the experimental determination of atomic numbers, which

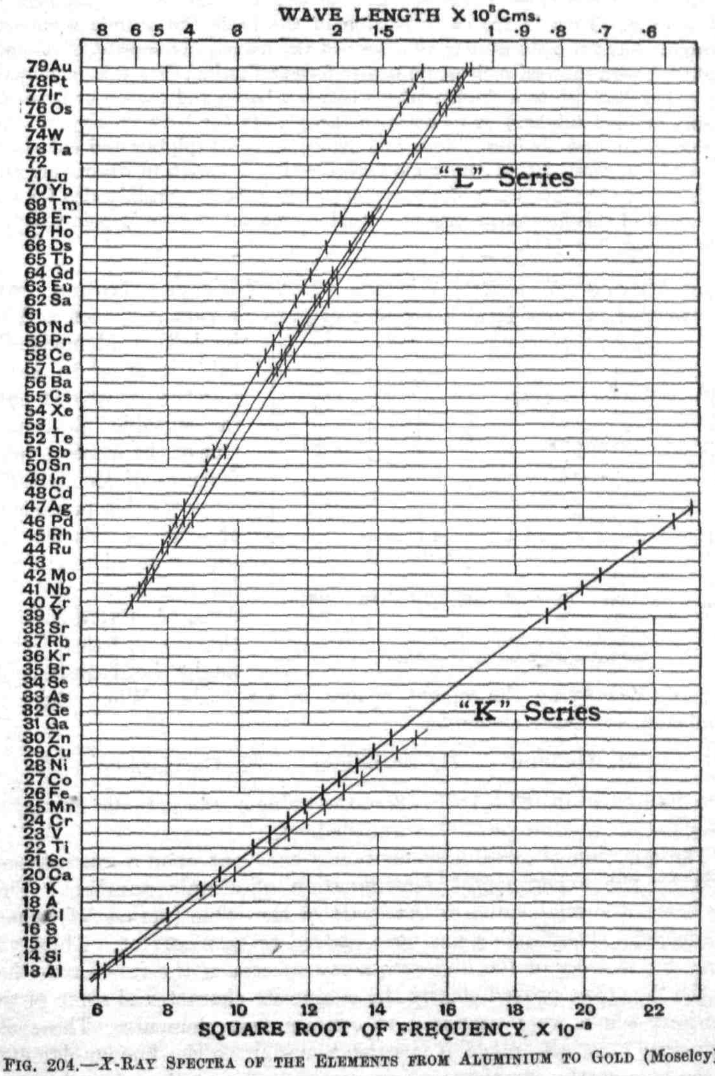


FIG. 204.—*X*-RAY SPECTRA OF THE ELEMENTS FROM ALUMINIUM TO GOLD (Moseley).

places cobalt immediately after iron and nickel immediately before copper, in close agreement with the chemical relationships of these elements. In the same way, the study of the *X*-ray spectra from

cadmium to barium (Fig. 205) has shown that tellurium must precede iodine, instead of following it.

The exact relationship between atomic weights and atomic numbers is still obscure. Thus in the early portion of the table the atomic weight is approximately twice the atomic number and the average increment of atomic weight between successive elements is therefore two units; but this increment may either diminish to a single unit (as between boron and carbon or between phosphorus and sulphur) or increase to three units (as between oxygen and fluorine, neon and sodium, silicon and phosphorus, or sulphur and chlorine). It may be suggested that the same factor which is active in destroying the regularity of the increments of atomic weight may be responsible also for the conversion of this increment into an actual decrement at certain points in the table (see pp. 540–544).

(*b*) *Missing Elements.*—Whereas Newlands's classification was overcrowded, a considerable number of gaps or vacant spaces had to be left in Mendeléeff's table in order to maintain the known elements in suitable positions. One of the most notable features of Mendeléeff's work was his prediction of the existence of unknown elements to fill the gaps, and his detailed statements of the properties that might be expected in elements occupying the vacant spaces in his table. When three of Mendeléeff's missing elements,

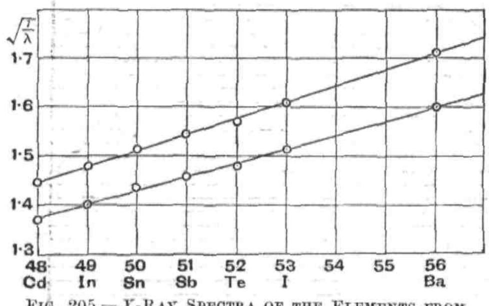


FIG. 205.—*X*-RAY SPECTRA OF THE ELEMENTS FROM CADMIUM TO BARIUM (Siegbahn).

31. *Gallium* 21. *Scandium* 32. *Germanium*

were discovered in 1875, 1879, 1886, the value of the periodic system of classification was universally acknowledged.

The question of missing elements has been put upon a much firmer basis by the experimental determination of atomic numbers. This has been of special value in that part of the table (period VI) where Mendeléeff's classification has been proved to be incorrect. Thus, the study by Moseley of the high-frequency spectra of the rare earths has for the first time proved clearly the composite character of some of the fractions which were supposed to contain new elements. These experiments have also made it possible to assign to the known elements of the rare earths atomic numbers covering almost the whole interval from 56. Barium to 73. Tantalum, as set out in Table 62. This interval (with the exception of two missing elements, 61 and 72) is now covered by 14 rare earth elements, all belonging to the aluminium family, and

the whole of one long period in Mendeléeff's classification has been suppressed in favour of this single cluster of elements. The missing elements between 1. Hydrogen and 92. Uranium are then reduced to 8, as shown in Table 62.

TABLE 62.—ATOMIC NUMBERS OF RARE-EARTH ELEMENTS AND MISSING ELEMENTS.

Rare-earth Elements			*Missing Elements*
57. Lanthanum	La	139·0	43. *eka*-Manganese
58. Cerium	Ce	140·25	61. A "rare earth"
59. Praseodymium	Pr	140·9	75. *dwi*-Manganese
60. Neodymium	Nd	144·3	84. *eka*-Tellurium
61. —	—	—	85. *eka*-Iodine
62. Samarium	Sa	150·4	87. *eka*-Cæsium
63. Europium	Eu	152·0	89. A radio-active earth
64. Gadolinium	Gd	157·3	91. *eka*-Tantalum
65. Terbium	Tb	159·2	
66. Dysprosium	Ds	162·5	*eka* = the *first* element after
67. Holmium	Ho	163·5	*dwi* = the *second* element after
68. Erbium	Er	167·7	*tri* = the *third* element after
69. Thulium	Tm	168·5	These prefixes are the Sanskrit numerals as used by Mendeléeff to describe the missing homologues of known elements.
70. Ytterbium	Yb	173·5	
71. Lutecium	Lu	175·0	

Radio-elements.

The fragment of a period which concludes Table 61 contains the radio-active elements.

86. Niton, 88. Radium, 90. Thorium, 92. Uranium.

These elements emit powerful radiations, apparently as a result of a spontaneous disintegration of the atoms (see Chapter XLV), but apart from this they exhibit normal chemical properties corresponding with the families of elements to which they belong. Thus **niton**, formerly known as RADIUM EMANATION, is a gas which, in spite of its intense activity, does not form any chemical compounds, and is therefore placed correctly, like the members of the helium family, at the commencement of the period. **Radium**, which is present to the extent of about 1 part in ten million of pitchblende, is a homologue of barium, and is thrown down with this element when it is precipitated as a sulphate. Again, **thorium** is a quadrivalent metal, which is obviously a homologue of germanium, and **uranium** is a natural homologue of molybdenum and tungsten.

By means of electrical measurements a large number of more transient RADIO-ELEMENTS, derived from uranium and thorium by disintegration, have been detected in the range of atomic weights extending

cadmium to barium (Fig. 205) has shown that tellurium must precede iodine, instead of following it.

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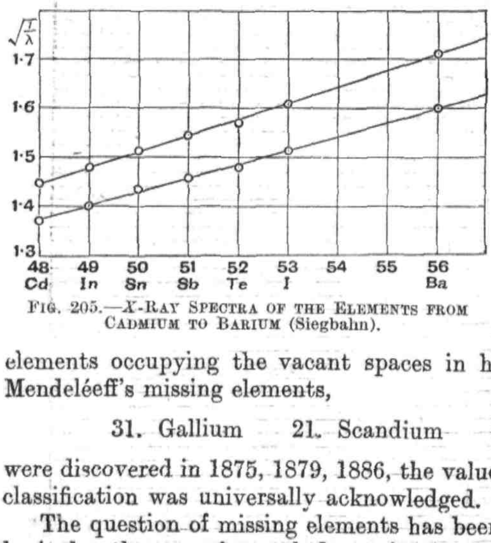

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By means of electrical measurements a large number of more transient RADIO-ELEMENTS, derived from uranium and thorium by disintegration, have been detected in the range of atomic weights extending

The positive-ray spectrum indicates the transient existence of many molecules which are not known as stable compounds. Thus Fig. 208, *I*, shows a series of lines from 24 to 32, most of which are attributed to C_2 compounds, each with a single positive charge, as follows :—

$C_2 = 24$, $C_2H = 25$, $C_2H_2 = 26$, $C_2H_3 = 27$, C_2H_4 or CO or $N_2 = 28$, $C_2H_5 = 29$, $C_2H_6 = 30$.

Above these, and in Fig. 208, *II*, are seen some of the lines of the C_1 series :

$C_1 = 12$, $CH = 13$, CH_2 (or N) $= 14$, $CH_3 = 15$, CH_4 or $O = 16$, $HO = 17$, $H_2O = 18$.

In addition, Fig. 208, *I*, shows a line due to $O_2 = 32$, and Fig. 208, *III*, shows $CO_2 = 44$, whilst Fig. 208, *IV*, shows groups of lines at 50 and $66\frac{2}{3}$, due to mercury atoms with four and three charges Hg^{++++} and Hg^{+++}.

The isotopes of neon, Ne^{20} and Ne^{22}, are seen at 20 and 22 in Fig. 208, *I*, these integral atomic weights being probably correct within $\pm 0{\cdot}02$, or 0·1 per cent. The isotopes of chlorine, Cl^{35} and Cl^{37}, are seen with double charges at 17·5 and 18·5 in Fig. 208, *II*; Fig. 208, *III* (which shows the presence of Ne still in the tube), contains a group of four lines at 35, 36, 37, 38, due to the two isotopes of chlorine, Cl^{35} and Cl^{37}, together with their hydrides, HCl^{35} and HCl^{37}; these four lines are seen also in Fig. 208, *IV*, with two lines at 63 and 65 are due to the radicals $COCl^{35}$ and $COCl^{37}$, the gas used in the apparatus being carbonyl chloride, $COCl_2$.

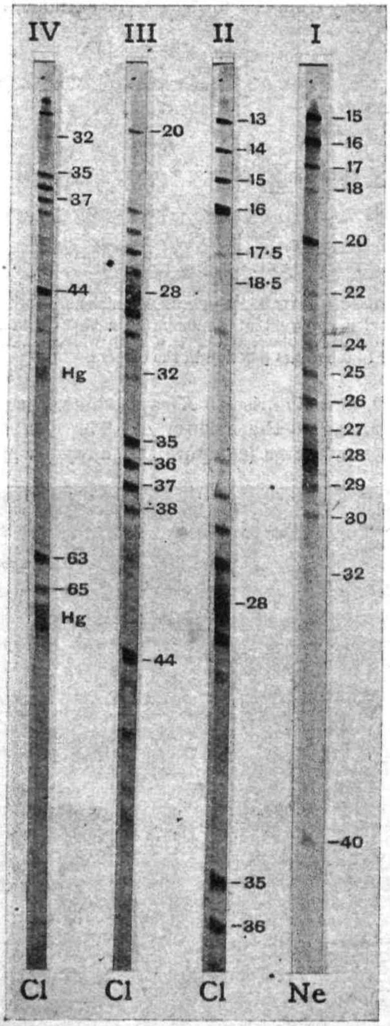


FIG. 208.—MASS SPECTRA (Aston).

A list of some elements (outside the radioactive series) which have been tested for the presence of isotopes in the method described above is given in Table 63. A modified method has shown that the alkali metals contain the following constituents : Li, 6·7 ; Na, 23 only ; K, 39, 41 ; Rb, 85, 87 ; Cs, 133 only.

TABLE 63.—ELEMENTS AND ISOTOPES.

Element.	*Atomic number.*	*Atomic weight.*	*Minimum number of constituents.*	*Masses of isotopes in order of their intensity.*
H	1	1·008	1	1·008
He	2	3·99	1	4
B	5	10·90	2	11, 10
C	6	12·00	1	12
N	7	14·01	1	14
O	8	16·00	1	16
F	9	19·00	1	19
Ne	10	20·20	2	20, 22, (21)
Si	14	28·30	2	28, 29, (30)
P	15	31·04	1	31
S	16	32·06	1	32
Cl	17	35·46	2	35, 37, (39)
A	18	39·88	2	40, 36
As	33	74·96	1	75
Br	35	79·92	2	79, 81
Kr	36	82·92	6	84, 86, 82, 83, 80, 78
I	53	126·92	1	127
Xe	54	130·32	5 (7)	129, 132, 131, 134, 136 (128, 130 ?)
Hg	80	200·60	(6)	(197–200), 202, 204

(Numbers in brackets are provisional only.)

Prout's Hypothesis and the Whole Number Rule.

Following closely upon the first correct determination of the density of hydrogen, Prout in 1816 revived the old hypothesis that all matter was derived from a primordial element, or PROTYLE (Greek, πρώτη ὕλη, first matter), and suggested that hydrogen was the true protyle and that all atomic weights were integral multiples of the atomic weight of hydrogen. It has already been pointed out (pp. 112 and 120) that PROUT'S HYPOTHESIS of integral atomic weights is much more nearly realised when $O = 16$ exactly and $H = 1{\cdot}008$ than when $H = 1$ exactly and $O = 15{\cdot}88$, and that with the former standard integral atomic weights are observed with surprising frequency.

By far the most important generalisation resulting from the study of the mass-spectra of the elements is that the mass of every atom so far examined is a whole number on the oxygen scale, within a few hundredths of a unit, and it is extremely probable that this is true of all elements. The reason why so many elements give atomic weights approximating to whole numbers is now clear. All simple elements consisting of atoms of one kind may be expected to do so, while, in

addition, complex elements may, by the ordinary law of probability, give atomic weights approximating to whole numbers. The latter is actually the case with the element bromine, which is found to consist of isotopes of atomic weights 79 and 81 in about equal quantities, its chemical atomic weight being very nearly 80.

The case of hydrogen is of particular interest, as it is so far the only element the divergence of which from the whole number rule is measurable. The value obtained is in good agreement with that already accepted by chemists, and there are theoretical reasons why it may be definitely greater than unity on the oxygen scale.

The Nucleus Atom.

The whole number rule confirms in a simple and satisfactory manner the old idea that the atoms of all elements are built up of primordial atoms grouped together in various numbers. Two kinds of primordial atoms are now postulated, namely, positive atoms of electricity, or PROTONS, and negative atoms of electricity, or ELECTRONS. The former are enormously the heavier, so that the weight of the latter may usually be neglected.

An atom is supposed by Rutherford to consist of a small but heavy NUCLEUS, made of protons and electrons packed closely together and surrounded, at a distance great compared with its diameter, by a number of PLANETARY ELECTRONS. According to this view hydrogen is the simplest element possible, consisting of a single proton of weight 1 approximately * and a single planetary electron revolving round it. When converted into a hydrogen ion, by losing its electron, it consists of a single proton only. The atomic weight of an element is determined by the total number of protons in the nucleus ; on the other hand, the excess of protons over electrons in the nucleus of the atom, which is clearly equal to the number of planetary electrons when the atom is electrically neutral, is the ATOMIC NUMBER of the element, and determines all its chemical properties. Thus an atom of fluorine has a nucleus made up of 19 protons and 10 electrons, round which are spaced 9 planetary electrons ; its atomic number is therefore 9 and its atomic weight 19. It is apparently impossible to have a nucleus containing less than one electron to each two protons, except in the case of hydrogen ; the atomic weight is therefore either equal to twice the atomic number, as in the case of He, C, N, O and Ne^{20}, or greater, as in the case of F, Ne^{22}, Cl^{35}, Cl^{37}, etc. An atom of weight $m + 1$ may be made from an atom of weight m by adding one proton and one electron. If both enter the nucleus, an isotope results, for the nuclear charge, and therefore the atomic number, of the element is

* There are reasons for thinking that the effective mass of the proton may be greater, *e.g.*, in the ratio 1·008 : 1, when free or associated only with a planetary electron than it is when associated closely with electrons in the nucleus of an atom.

unaltered, although its atomic weight is increased by one unit. If the proton only enters the nucleus, an atom of next higher atomic number is formed. If both these configurations are stable we shall have two elements of identical atomic weight but different chemical properties. Such elements are actually found in the radioactive series and are called ISOBARES.

Periodic and Non-periodic Properties.

Lothar Meyer in 1869 defined the LAW OF PERIODICITY as follows :

> " The properties of the elements are largely *periodic* functions of the atomic weight. Identical or similar properties recur, if the atomic weight is increased by a definite amount, which is at first 16, then about 46, and finally 88 to 92 units."

Thus, the series

$$Li = 7, \quad Na = 23, \quad K = 39, \quad Rb = 85, \quad Cs = 133$$

shows differences of 16, 16, 46, and 48 ; the series

$$F = 19, \quad Cl = 35\tfrac{1}{2}, \quad Br = 80, \quad I = 127$$

shows differences of $16\frac{1}{2}$, $44\frac{1}{2}$, and 47 ; and the series

$$N = 14, \quad P = 31, \quad As = 75, \quad Sb = 120, \quad Bi = 208$$

shows differences of 17, 44, 45, and 88.

(*a*) *Atomic Volume and Atomic Radius.*—The ATOMIC VOLUME of an element is defined by the equation

$$\textit{specific volume} \times \textit{atomic weight} = \textit{atomic volume},$$

where the SPECIFIC VOLUME is the volume occupied by 1 gram of the element ; it may also be defined as the volume in cubic centimetres occupied by the atomic weight of the element expressed in grams. When this property was plotted by Meyer, he obtained a curve showing a series of waves or periods (Fig. 209), which still forms one of the best illustrations of the law of periodicity. This curve reveals clearly the natural grouping of the elements into two short periods, II and III, followed by two long periods, IV and V ; but, like Mendeléeff, Meyer assumed that these two long periods would be followed by two more long periods of a similar type. He therefore showed in his diagram two hypothetical peaks, corresponding with unknown elements of the lithium family, thus dividing the sixth period of Table 61 into two long periods. For this subdivision, no experimental evidence has yet been found, and the curve of Fig. 209 therefore shows only one instead of two waves or periods in the range of elements from cæsium to niton.

The atomic volume curve forms a very convenient method of classifying the elements, since *elements occupying similar positions on the atomic volume curve tend to exhibit similar properties.* Thus, in the original curve all the crests were occupied by the elements of the alkalies, although some of these have since been usurped by inert gases

of the helium family. The halogens appear on the slopes immediately before each crest and the alkaline earths on the slopes immediately beyond. The heavy metals, which play so important a part in industry, are naturally found in the troughs of the curves This representation has the advantage that there is here no indication that sodium and copper should be grouped together as members of one family, since they occupy entirely different positions on the curve, corresponding with their totally different physical and chemical properties.

The atomic volumes of the solid and liquid elements as plotted by Lothar Meyer make no allowance for the way in which the atoms

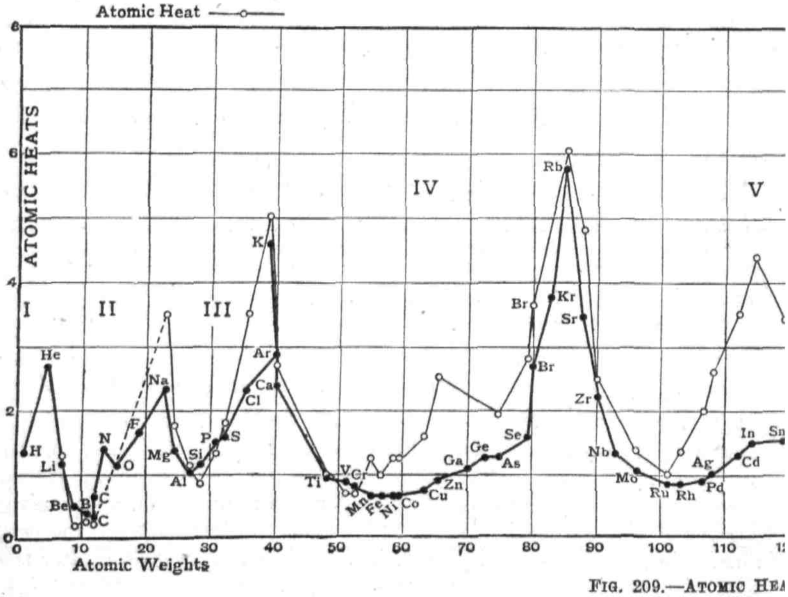


FIG. 209.—ATOMIC HEA

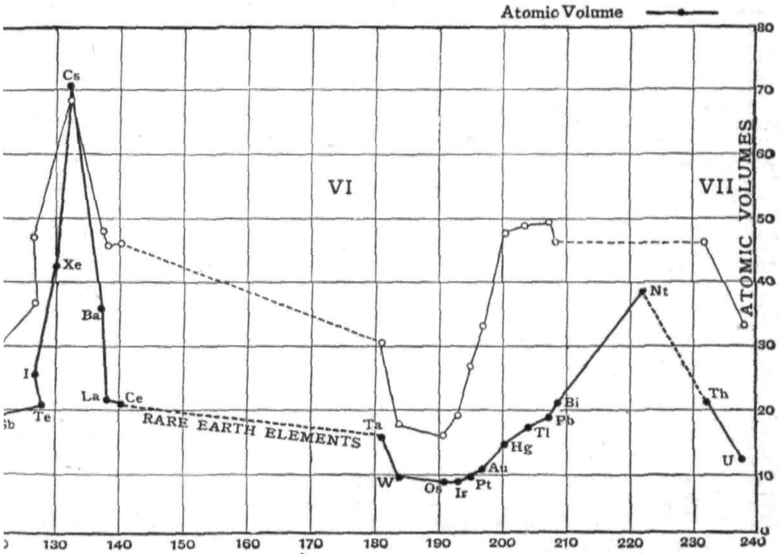
are packed together. Bragg's work on the analysis of crystal-structure by *X*-rays (p. 215) has, however, led him to the conclusion that each element has a definite ATOMIC RADIUS, such that two atoms cannot approach nearer together in a crystal than the sum of their radii.

TABLE 64.—ATOMIC RADII OF THE ELEMENTS.

Li	1·50	Be	1·15			C	0·77	N	0·65	O	0·65	F	0·67
Na	1·77	Mg	1·42	Al	1·35	Si	1·17			S	1·02	Cl	1·05
K	2·07	Ca	1·70			Ti	1·40	As	1·26	Se	1·17	Br	1·19
Rb	2·25	Sr	1·95			Sn	1·40	Sb	1·40	Te	1·33	I	1·40
Cs	2·37	Ba	2·10			Pb	1·90	Bi	1·48				
Cr	1·40 / 1·17	Mn	1·47 / 1·17	Fe	1·40	Co	1·37	Ni	1·35	Cu	1·37	Zn	1·32
										Ag	1·77	Cd	1·60

These radii are plotted against the atomic numbers of the elements in Fig. 210 and show a very marked periodicity, the radii rising as in Lothar Meyer's curve to a series of maxima at the alkali metals, but then falling to an almost constant minimum in the latter part of each period. In the case of chromium and manganese, two values are given for the atomic radius, the higher values being used when the element functions as a metal, isomorphous with iron or nickel, and the lower value when it functions as a non-metal, isomorphous with sulphur or chlorine.

(*b*) *Specific and Atomic Heats.*—Amongst the very few properties which are not periodic, but vary continuously as the atomic weight is



ND ATOMIC VOLUMES.

increased, are the SPECIFIC HEATS of the solid and liquid elements at normal temperatures, and their ATOMIC HEATS as calculated from the equation

$$\textit{specific heat} \times \textit{atomic weight} = \textit{atomic heat}.$$

The law of Dulong and Petit represents the atomic heat of the solid elements as a constant; if plotted against the atomic weights, therefore, the atomic heats should be represented by a horizontal straight line. The specific heats, being in inverse proportion to the atomic weights, should give a rectangular hyperbola. This condition is realised, with a few exceptions, in the atomic heats of the elements at atmospheric temperatures and upwards, but a totally different condition prevails at lower temperatures. Thus, Dewar has shown that, in the

range from $-195°$ to $-253°$, the atomic heat diminishes to a fraction of its value at the ordinary temperature, and at the same time changes from a constant to a fully periodic property, the variations of which,

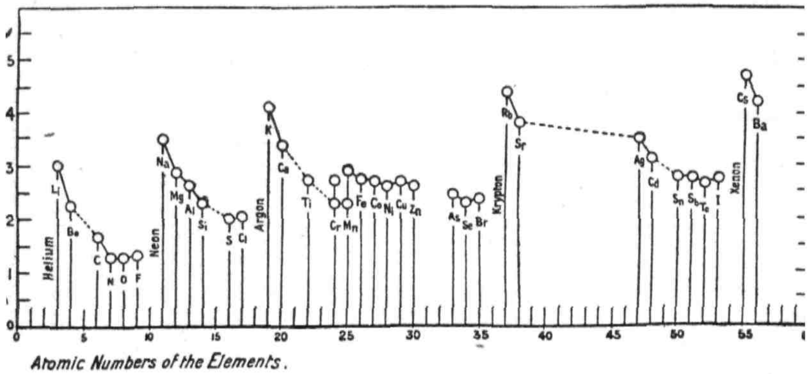


FIG. 210.—ATOMIC RADII OF THE ELEMENTS PLOTTED AGAINST THEIR ATOMIC NUMBERS.

as shown in Fig. 209, follow somewhat closely those of the atomic volumes plotted forty-four years before by Lothar Meyer.

(*c*) *Valency*.—Perhaps the most important of the periodic properties of the elements is their valency, which in the two short periods rises and falls in the regular manner indicated by the empirical formulæ set out in the following table :

TABLE 65.—VALENCY OF ELEMENTS IN TWO SHORT PERIODS.

(i) *Hydrides.*

Typical valency	0	1	2	3	4	3	2	1
Formula of hydride	He	LiH	BeR_2	BH_3	CH_4	NH_3	OH_2	FH
	Ne	NaH	MgR_2	AlR_3	SiH_4	PH_3	SH_2	ClH

Helium and neon do not form hydrides.
Beryllium, magnesium, and aluminium do not form hydrides, but form analogous compounds in which $R = CH_3$, C_2H_5, etc.

(ii) *Chlorides.*

Typical valency	0	1	2	3	4	3	2	1
Formula of chloride	—	LiCl	$BeCl_2$	BCl_3	CCl_4	NCl_3	OCl_2	—
	—	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	S_2Cl_2	Cl_2
						PCl_5	SCl_4	

(iii) *Oxides.*

Typical valencies	0	1	2	3	4	3 or 5	2 or 6	1 or 7
Formulæ of oxides	—	Li_2O	BeO	B_2O_3	CO	N_2O to	O_2	—
					CO_2	N_2O_5		
	—	Na_2O	MgO	Al_2O_3	SiO	P_2O_3	SO_2	Cl_2O
		Na_2O_2			SiO_2	PO_2	SO_3	ClO_2
						P_2O_5	S_2O_7	Cl_2O_7

The periodic rise and fall of valency shown in this table appears to be a normal characteristic of the two short periods. In the long periods,

the earliest and latest members of each period agree in valency (as well as in their other properties) with the earliest and latest members of the short periods and show the same regular gradation, *e.g.*,

Hydrides and *Chlorides*

0, 1, 2, 3, 4 – – – – – – – 4, 3, 2, 1

Oxides

0, 1, 2, 3, 4 – – – – – – – 4, 5, 6, 7 ;

but in the central portions of the long periods this rise and fall of valency is very largely masked by steady valencies of 2, 3, or 4 running right through the nine intermediate transition-elements (see below, p. 719).

The valencies of the elements are plotted against their atomic numbers in Fig. 211, the POSITIVE VALENCIES of the elements in their oxides and chlorides being shown above the zero line, and their NEGATIVE VALENCIES in combination with hydrogen and the metals below the zero line. This arrangement has the advantage of displaying clearly the tendency of the valency to increase as the atomic number rises, in addition to the tendency to assume a stationary value in the transition-elements and in the elements of the rare earths.

In spite of the many exceptions that occur, the regular variations of valency to which attention has just been directed are perhaps the most important feature of the periodic classification of the elements. Thus, equality of valency brings into harmony the formulæ of compounds derived from such widely different elements as nitrogen, phosphorus, and arsenic, and thus justifies the grouping together in one family of these very diverse elements. On the other hand, dissimilarity of valency produces a contrast in the formulæ of the compounds of sulphur and phosphorus which tends to disguise the very real resemblance between these two elements both in their physical and in their chemical properties.

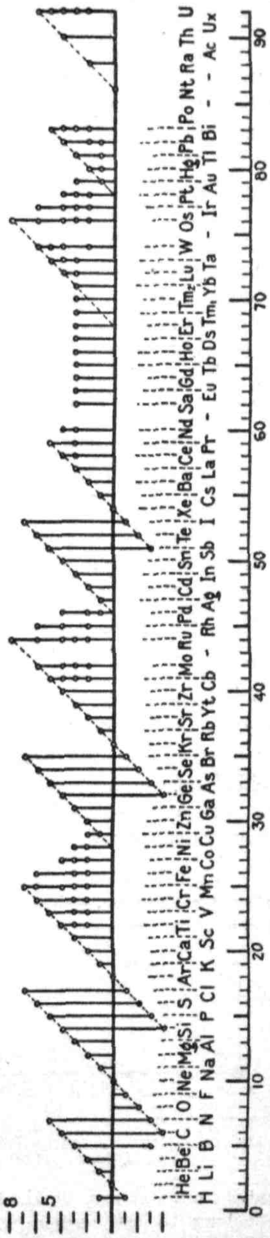


FIG. 211.—VALENCIES OF THE ELEMENTS (after Langmuir).

The Octet Theory.

The periodicity in the properties of the elements should evidently be capable of interpretation in terms of the nuclear atom when sufficient data have been accumulated to determine the atomic structure of the principal elements. Lewis and Langmuir have suggested that a maximum of stability is attained in the lighter elements when there are *two* electrons near the nucleus and an OCTET of *eight* electrons in an outer zone around it. Neon, therefore, with atomic number 10 (like helium with atomic number 2), is a neutral element which forms no compounds of any kind. Fluorine, with atomic number 9, very readily takes up an additional electron in order to complete the octet and enters into combination as a univalent anion, F^-, whilst sodium, with atomic number 11, loses an electron and enters into combination as a univalent cation, Na^+; in forming sodium fluoride, therefore, each element acquires the stable configuration of neon. Similar considerations can be used to account for the bivalency of oxygen and magnesium, thus

8. Oxygen, acquires 2 electrons and becomes O^{--}.
12. Magnesium, loses 2 electrons and becomes Mg^{++}.

Again, the valencies of the elements before and after argon, krypton, xenon, and niton may be attributed to a tendency to assimilate to the arrangement of planetary electrons in the inert gases, the successive zones or SHELLS of which contain 2, 8, 8, 18, 18, and 32 electrons.

On the basis of his theory that atoms are built up of electrons arranged in shells around a central nucleus, Langmuir distinguishes two types of valency, namely (i) ELECTROVALENCE, corresponding with the number of electrons which the atom must lose or gain in order to acquire the same stable grouping of electrons that is found in an atom of one of the inert gases, (ii) COVALENCE, whereby atoms are welded into molecules by pairs of electrons shared or held in common as part of the shell of two atoms; these pairs of electrons or DUPLETS represent the BONDS of structural chemistry (p. 149).

The combination of carbon, which has four electrons less than neon, with two oxygen atoms, each with two electrons less than neon, has been explained as due to an assimilation of the atoms in such a way that the four electrons in the outer zone of the carbon atom are shared with and form part also of the outer zones of the two oxygen atoms, giving rise to three "octets" as in Fig. 212, where the octets of electrons are represented for convenience as occupying the eight corners of a cube. Each atom is here assumed to have 2 electrons in an inner zone, whilst the three outer zones shown in the figure contain a total of 16 electrons, of which 4 belong to the carbon atom (atomic number = 6) and 2 × 6 = 12 to

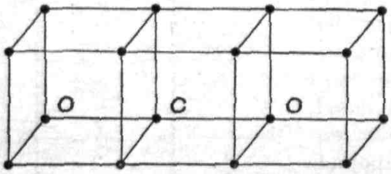


FIG. 212.—CARBON DIOXIDE REPRESENTED BY THREE OCTETS

the two oxygen atoms (atomic number = 8). Nitrous oxide, N_2O, can be represented by a precisely similar figure, the two nitrogen atoms (atomic number = 7) contributing 2 × 5 = 10, and the central oxygen atom (atomic number = 8) 6 electrons to the total of 16 electrons used in building up the three octets. These two gases are said to be ISOSTERIC (Greek, ἴσος, equal; στερεός, solid), since they contain the same number of electrons arranged in the same way in space; their physical properties are also almost identical (Table 46, p. 410). The molecules of isosteric compounds differ from one another in the weight of the nuclei of the various atoms and are related to one another in the same way as the atoms of isotopic elements.

Grouping of the Metals.

With the exception of arsenic, all the elements shown in heavy type in Table 61 have been described as non-metals in Part II above. In the case of the metals, it has been found convenient, following a distinction first made by Mendeléeff, to divide these elements into two main series, namely, (*a*) the TYPICAL SERIES, including those families the lower homologues of which find a place in the two short periods, and (*b*) the TRANSITION SERIES, including those elements which occupy the centres of the long periods, and have therefore no clear analogues in the two short periods. The metals are therefore described in the following chapters in groups selected from the periodic table as follows:

PART III. TYPICAL SERIES.

CHAPTER		
XXXII	*Metals of the Alkalies* . .	Li, Na, K, Rb, Cs, —.
XXXIII	*Metals of the Alkaline Earths* .	Be, Mg, Ca, Sr, Ba, Ra.
XXXIV	*Metals of the Earths* . .	Al and the elements of the rare earths.
XXXV	*Quadrivalent elements* [C] [Si]	Ti, Zr, — Th. Ge, Sn, Pb.
XXXVI	*The Arsenic Group* [N] [P]	As, Sb, Bi.

PART IV. TRANSITION SERIES.

XXXVIII	*Vanadium and its homologues*	V, Cb, Ta, —
XXXIX	*Chromium and its homologues*	Cr, Mo, W, U.
XL	*Manganese*	Mn, — — —
XLI	*Iron, Cobalt, and Nickel* . .	Fe, Co, Ni.
XLII	*Palladium and Platinum Triads.*	Ru, Rh, Pd, Os, Ir, Pt.
XLIII	*The Coinage Metals* . . .	Cu, Ag, Au.
XLIV	*The Mercury Group* . . .	Zn, Cd, Hg. with Ga, In, Tl.
XLV	*The Radio-elements.*	

CHAPTER XXXII

THE METALS OF THE ALKALIES

Atomic number.	*Element.*	*Symbol.*		*Atomic weight.*
3	Lithium	Li	=	6·94
11	Sodium	Na	=	23·00
19	Potassium	K	=	39·10
37	Rubidium	Rb	=	85·45
55	Cæsium	Cs	=	132·81

GENERAL PROPERTIES OF THE GROUP.

Physical Properties.

The metals of the alkalies occupy a conspicuous position at the commencement of each of the main periods of the periodic classification of the elements, immediately after the gases of the helium group. They are well-defined metals, but are remarkable for their low density, low melting-point, and relatively low boiling-point, as shown in the following table :

TABLE 66 —PHYSICAL PROPERTIES OF THE METALS OF THE ALKALIES.

	Density.	*Melting-point.*	*Boiling-point.*
Li . .	0·53	179°	above 1400°
Na . .	0·97	97·5	877
K . .	0·86	62·5	757
Rb . .	1·52	38·5	696
Cs . .	1·88	28	670

Each element of the group imparts a characteristic colour to the flame and gives rise to a FLAME-SPECTRUM, consisting of a few prominent lines by means of which very minute traces of the element can be detected. It was indeed by their flame-spectra that rubidium and cæsium were first discovered, and in the case of lithium and sodium the characteristic lines are strong enough, and sufficiently pure, to be used as sources of monochromatic red and yellow light in optical experiments

TABLE 67.—FLAME-SPECTRA OF THE ALKALIES.

Element.	*Flame-colour.*	*Spectrum lines.**
Lithium . .	Red	6708 (red).
Sodium . .	Yellow	5896 and 5890 (a yellow doublet).
Potassium . .	Violet	7702 and 7668 (deep red).
Rubidium . .	Red	6299 (red).
Cæsium . .	Blue	4593 and 4555 (blue doublet).

Chemical Properties.

(*a*) *Valency.*—The metals of the alkalies are all univalent elements, forming *hydrides*, *chlorides*, and *oxides* of the formulæ MH, MCl, and M_2O, and *nitrates*, *sulphates*, and *phosphates* of the formulæ MNO_3, M_2SO_4, and M_3PO_4. Compounds of abnormal valency are practically limited to *peroxides* such as Na_2O_2, K_2O_2, and K_2O_4, and *per-halogen compounds* such as KI_3, $RbBr_3$, and CsI_5. Even in the peroxides, the metal is probably still univalent, as shown in the formula Na—O—O—Na, compare Na—O—Na. In the same way, in the per-halogen compounds, it is probably the "residual affinity" of the iodine, and not any increase in the valency of the potassium, which enables potassium iodide, KI, to unite with a molecule of iodine, I_2, to form the periodide, KI_3.

(*b*) *Combination with Non-metals.*—The elements of this group are remarkable for their great chemical activity. They oxidise rapidly on exposure to air, and decompose water, liberating hydrogen and giving rise to strongly alkaline hydroxides, *e.g.*,

$$2Na + 2H_2O = 2NaOH + H_2$$
$$2K + 2H_2O = 2KOH + H_2;$$

they are therefore usually stored in contact with paraffin, although lithium floats on this liquid instead of sinking in it. When heated in air or oxygen, they take fire and burn to oxides or peroxides. They also burn in chlorine, unless absolutely dry, giving rise to chlorides of the type of common salt, *e.g.*,

$$2Na + Cl_2 = 2NaCl.$$

(*c*) *Solubility of Salts.*—The salts of these elements are remarkable for their solubility in water. A few of the lithium salts and some of the less common salts of the other elements are, however, sparingly soluble in water and can be used in detecting and separating the elements of this group, *e.g.*, potassium perchlorate, $KClO_4$, potassium platinichloride, K_2PtCl_6, potassium cobaltinitrite, $K_3Co(NO_2)_6$, sodium metantimonate, $Na_2H_2Sb_2O_7,6H_2O$, and finally the ternary nitrite, $6NaNO_2,9CsNO_2,5Bi(NO_2)_3$, by means of which sodium can be separated quantitatively from the other elements of the group.

* The wave-lengths are given in Ångström units, *i.e.*, 10^{-8} cm.

11. SODIUM. Na = 23·00.

Occurrence of Sodium.

On account of the great readiness with which it interacts both with oxygen and with water, sodium is never found in the free state. In combination, however, it is one of the six common metals which with silicon and oxygen make up about 97 per cent. of the outer surface of the earth, thus:

O 50%	Al 7%	Ca 3%	Na 2½%
Si 26%	Fe 4%	Mg 2%	K 2½%

(*a*) *Salt.*—The principal source of sodium and its compounds is COMMON SALT or **sodium chloride**, $NaCl$, which is present to the extent of 3 per cent. in sea-water, and can be extracted from it in the form of SEA-SALT by evaporation; it is also found in extensive mineral deposits, formed by the evaporation of prehistoric seas, and is mined under the name of ROCK-SALT. The total quantity of sea-salt in the ocean is estimated to be 5 million cubic miles, equivalent to a layer more than 100 feet thick on the whole surface of the earth.

(*b*) *Felspar.*—The sodium in igneous rocks is present mainly as **sodium alumino*tri*silicate** in the form of SODA FELSPAR or ALBITE, $NaAlSi_3O_8$ (p. 503), but in lavas it may appear with a smaller proportion of silica as **sodium alumino*mono*silicate**, $NaAlSiO_4$, *e.g.*, in NEPHELITE, (p. 507). Sodium and aluminium also appear together as **sodium aluminofluoride**, Na_3AlF_6, in CRYOLITE (p. 659), a mineral which has perhaps been formed by the action on felspar of volcanic gases containing fluorine.

(*c*) *Soda.*—By the action of water and carbon dioxide on felspar, much of the sodium is removed in the form of **sodium carbonate**, Na_2CO_3, leaving behind a mixture of kaolinite, or clay, and silica,

$$\underset{\text{Felspar}}{2NaAlSi_3O_8} + 2H_2O + CO_2 = Na_2CO_3 + \underset{\text{Kaolinite}}{H_4Al_2Si_2O_9} + 4SiO_2.$$

This soda is usually carried down by rivers to the ocean, but in desert regions, or in regions without an outlet to the ocean, it accumulates, giving rise to alkaline lakes, such as the SODA LAKES of Egypt, Lake Magadi in East Africa, and the Great Salt Lake of Utah, or to dry beds encrusted with TRONA or **sodium sesquicarbonate**, $Na_2CO_3,NaHCO_3,2H_2O$. The calcium salts entering a soda lake are usually precipitated in a crystalline form as GAYLUSSITE or **sodium calcium carbonate**, $CaCO_3,Na_2CO_3,5H_2O$, or $Ca(CO_3Na)_2,5H_2O$, the sodium salt of calcium bicarbonate, $Ca(CO_3H)_2$. Soda is also present in the ash of sea plants, and **sodium carbonate**, Na_2CO_3, was formerly manufactured from this source as BARILLA for making soap.

(*d*) *Borax.*—The alkaline lakes referred to in the preceding paragraph often contain boric acid, especially where the waters are derived in part from hot springs in volcanic districts. The boric acid in

these springs is present largely as ammonium borate, but crystallises out as BORAX or **sodium pyroborate**, $Na_2B_4O_7,10H_2O$, in the soda lakes.

(*e*) *Chile Saltpetre.*—The deserts of Atacama and Tarapaca, on the borders of Chile and Peru, contain very extensive deposits of **sodium nitrate**, $NaNO_3$, in the form of CALICHE or CHILE SALTPETRE, which are of value mainly on account of the "fixed nitrogen" (p. 361) which they contain. These deposits are constantly associated with borax and contain iodine in the form of **sodium iodate**, $NaIO_3$; but they are usually free from bromides and phosphates and cannot therefore have come from sea-water or from guano. The nitrogen is probably of organic origin, and may represent an extraction and concentration by occasional tropical floods of the fixed nitrogen from fertile soils; but the association of boric acid and ammonia in hot springs and of borates and nitrates in the nitrate-beds has led to the suggestion that boron nitride, BN, may be the parent substance from which the compounds of both elements have been derived.

METALLIC SODIUM.

Preparation of Metallic Sodium.

(*a*) *By Electrolysis.*—Sodium was first prepared by Davy in 1807 by the electrolysis of sodium hydroxide,

$$NaOH = Na + OH \text{ or } 4NaOH = 4Na + 2H_2O + \underset{\text{(at the anode)}}{O_2}$$

This process was abandoned for a time in favour of reduction by carbon, but is now again universally adopted for the commercial preparation of the metal.

Fig. 212 shows the arrangement used in working the CASTNER PROCESS. The sodium hydroxide, *a*, is contained in an iron bath and is melted initially by gas burners at *g*, but is afterwards retained in a molten condition by the heating-effect of the current used for electrolysis. The metal cathodes, *h*, are led into the bath from below through pipes, as at *b*, from which they are insulated by solidified sodium hydroxide as at *k*; they are surrounded by iron gauze, *m*, suspended from an iron cylinder, *c*, in which metallic sodium collects, as at *d*. The anodes, *f*, are of nickel to resist oxidation; they surround the cathodes and form part of the cover, being insulated by asbestos, *ss*, from the iron bath and from the iron cylinders, *c*. The oxygen set free at the anode escapes at *p*, whilst the hydrogen set free at the kathode escapes round the edges of the cover, *n*. This cover is lifted from time to time, and the sodium removed by a ladle of nickel gauze, in which the metal is retained on account of its high surface tension, whilst the hydroxide flows back into the bath. The bath holds about 100 kg. of sodium hydroxide and uses a current of 1200 amperes at 5 volts. To ensure a good yield the temperature should be kept within 20° of the melting-point of sodium hydroxide at 318°.

The ideal method of preparing sodium would be by a direct electrolysis of sodium chloride,

$$2NaCl = 2Na + Cl_2.$$

This would eliminate

(i) the intermediate preparation of sodium hydroxide from salt,
(ii) the burning away of the carbon anodes (when used) by oxygen,
(iii) the liberation at the anode of water, which tends to work across to the cathode, and to decompose half of the sodium originally set free by the current.

The principal difficulties of this method arise from the high melting-point of the salt, the volatility and inflammability of sodium at such high temperatures, and the corrosive action both of metallic sodium and of molten salt on the vessels in which electrolysis must be carried out. In order to overcome these difficulties, it has been proposed to prepare sodium by the electrolysis of molten salt between a carbon anode which receives the chlorine and a cathode of molten lead which absorbs the sodium as fast as it is formed; the lead-sodium alloy is then circulated into another vessel containing fused sodium hydroxide, which is electrolysed, at a much lower temperature, between the lead, which now becomes an anode and gives up its sodium, and an iron cathode in contact with which an equivalent quantity of sodium is set free. Experiments have also been made with the view of preparing sodium by the direct electrolysis of a mixture of sodium chloride and sodium carbonate, which melts at a much lower temperature than pure salt.

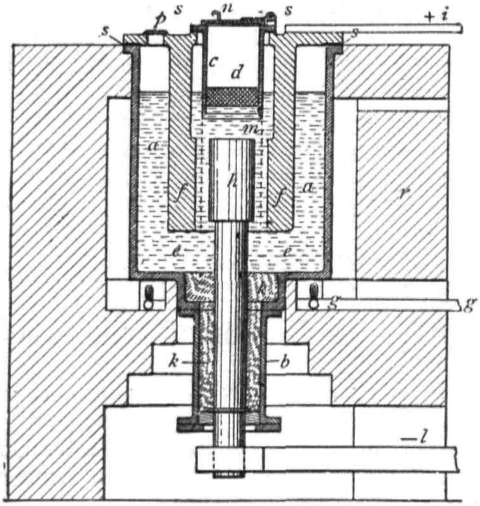


FIG. 213.—CASTNER PROCESS FOR PREPARATION OF SODIUM.

(*b*) *By Reduction.*—Gay-Lussac and Thénard in 1811 prepared sodium by reducing sodium hydroxide with iron,

$$2Fe + 2NaOH = 2FeO + 2Na + H_2.$$

Deville, in 1855, introduced a commercial reduction-process in which sodium was prepared by distilling sodium carbonate with carbon and a small proportion of chalk,

$$Na_2CO_3 + 2C = 2Na + 3CO.$$

In the Castner process, this method of preparation was again modified by heating sodium hydroxide with a carbide of iron,

$$FeC_2 + 6NaOH = 2Na + 2Na_2CO_3 + 3H_2 + Fe.$$

In view of the great affinity of sodium for oxygen, it may be assumed that the reduction of its oxide by iron and carbon depends on the fact that sodium can be distilled out from these mixtures, whilst iron and carbon cannot be distilled under similar conditions.

Uses of Metallic Sodium.

Metallic sodium was formerly used in the manufacture of aluminium and magnesium, but these are now prepared directly by electrolysis. It was also used until recently to prepare cyanides from ferrocyanides,

$$2Na + K_4FeC_6N_6 = 2NaCN + 4KCN + Fe.$$

At the present time, sodium is used mainly as a reducing agent, especially in organic chemistry, and for the preparation of sodamide (p. 558) and of sodium peroxide (p. 564).

Physical Properties of Sodium.

Sodium is a light, soft metal, which can be squeezed through a die in the form of sodium wire. It is a good conductor of heat and of electricity, its conductivity being almost one-third of that of silver. The density (0·97), melting-point (98°), and boiling-point (877°) of the metal have already been tabulated in comparison with other elements of the group.

Chemical Properties of Sodium.

(*a*) *Oxidation.*—When freshly cut, sodium shows a brilliant, white, metallic surface; but it tarnishes quickly in damp air owing to oxidation. It is therefore stored in the laboratory under paraffin, but on a commercial scale is sent out in small ingots enclosed in soldered tins. It burns in air with a bright yellow flame, giving a mixture of Na_2O and Na_2O_2. It floats upon water and is immediately decomposed by it, liberating hydrogen and forming sodium hydroxide, NaOH,

$$2Na + 2H_2O = 2NaOH + H_2.$$

If allowed to move freely, the metal does not ignite, but if stopped it bursts into flame, and large pieces are liable to produce explosion.

(*b*) *Displacement of Hydrogen by Sodium.*—Sodium dissolves quietly in alcohol, displacing hydrogen and forming sodium ethoxide, $NaOC_2H_5$,

$$2C_2H_5{\cdot}OH + 2Na = 2C_2H_5{\cdot}ONa + H_2;$$

the action is analogous to the decomposition of water by sodium, but the heat evolved is much less. Since sodium ethoxide is decomposed by water, as shown in the equation

$$C_2H_5{\cdot}ONa + H_2O = C_2H_5{\cdot}OH + NaOH,$$

standard solutions of sodium hydroxide can be prepared very conveniently by dissolving a known weight of sodium in alcohol and diluting with water to a definite volume. Sodium will also displace

hydrogen from ammonia and from acetylene (see below) and from many other compounds which are not acids and do not form salts even with caustic alkalies; the products, which are usually decomposed by water, are described as SODIUM-DERIVATIVES.

(c) *Chlorination.*—Sodium is not attacked by dry chlorine, but in damp chlorine it burns to common salt or sodium chloride, $NaCl$; common salt is also formed when sodium is used as a reducing agent to liberate metals such as magnesium and aluminium from their chlorides,

$$MgCl_2 + 2Na = Mg + 2NaCl.$$

These two methods of preparation are now obsolete, but metallic sodium is still used in the laboratory for the preparation of the more refractory elements from their chlorides and fluorides, *e.g.*,

Cerium, $CeCl_3 + 3Na = 3NaCl + Ce.$
Thorium, $K_2ThCl_6 + 4Na = 2KCl + 4NaCl + Th.$

(d) *Combination with Hydrogen.*—By heating sodium in a current of dry hydrogen in an iron vessel at 360° to 430°, **sodium hydride**, NaH, is obtained in the form of slender, transparent needles. It was formerly represented as Na_2H, but further study has shown that it has the composition and properties of a univalent hydride.

When heated in a vacuum it dissociates. Water decomposes it, giving sodium hydroxide and hydrogen,

$$NaH + H_2O = NaOH + H_2.$$

Dry ammonia at atmospheric temperatures converts it into sodamide (see below),

$$NaH + NH_3 = NaNH_2 + H_2.$$

Carbon dioxide in presence of a trace of water combines with it to produce sodium formate,

$$NaH + CO_2 = H{\cdot}CO{\cdot}ONa,$$

and sulphur dioxide converts it into sodium hydrosulphite,

$$2NaH + 2SO_2 = Na_2S_2O_4 + H_2.$$

(e) *Action on Nitrogen and on Ammonia.*—Sodium has no action on gaseous nitrogen, but under the influence of an electric discharge a **nitride** is said to be formed (compare the action of active nitrogen, p. 363), as a brown deposit which gives ammonia when decomposed by water. Its composition has not been determined, but its behaviour towards water suggests that its formula would probably be Na_3N.

Liquid ammonia dissolves sodium without liberation of gas, giving a blue solution which probably contains an additive compound, *e.g.*, $NH_3{\cdot}Na$. Substitution of sodium for hydrogen takes place, however, instead of addition, when sodium is heated in a current of dry ammonia at 300° to 400° in an iron vessel, giving rise to **sodamide**, $NaNH_2$,

$$2Na + 2NH_3 = 2NaNH_2 + H_2.$$

Sodamide melts at 155° to a colourless liquid, and volatilises at about 400°, condensing as a crystalline mass. It is decomposed by water with great evolution of heat, the action taking place often with explosive violence,

$$NaNH_2 + H_2O = NaOH + NH_3.$$

It is employed in many synthetical operations, often as a substitute for metallic sodium, and was formerly used for the preparation of sodium cyanide,

$$NaNH_2 + C = NaCN + H_2.$$

(*f*) *Action on Acetylene.*—When sodium is heated in a current of acetylene at 190°, or when acetylene is passed into a solution of sodium in anhydrous liquid ammonia (compare p. 451), **sodium acetylide**, C_2HNa, is formed,

$$2Na + 2C_2H_2 = 2C_2HNa + H_2.$$

$$2NH_3Na + 2C_2H_2 = C_2HNa + NaNH_2 + C_2H_4 + NH_3.$$

It decomposes at 210°, giving **sodium carbide**, Na_2C_2, and acetylene,

$$2C_2HNa = C_2H_2 + C_2Na_2.$$

COMPOUNDS CONTAINING HALOGENS.

Sodium Chloride.

(*a*) *Sea-salt.*—Sea water contains about 3½ per cent. of salts as follows:

TABLE 68.—COMPOSITION OF SEA-WATER.

Water	= 96·4 per cent.		or, roughly,	
NaCl	= 2·8 ,,		Common salt	= 2·8 per cent.
KCl	= 0·08 ,,		Magnesium salts	= 0·6 ,,
$MgCl_2$	= 0·37 ,,		Calcium salts	= 0·1 ,,
$MgSO_4$	= 0·23 ,,		Potassium salts	= 0·1 ,,
$CaSO_4$	= 0·14 ,,			
			Total salts	3·6 ,,

When sea-water is evaporated, the following salts can be separated from it:

(i) CHALK, $CaCO_3$, and GYPSUM, $CaSO_4,2H_2O$.
(ii) COMMON SALT, NaCl.
(iii) EPSOM SALTS, $MgSO_4,7H_2O$, and SCHÖNITE, $Mg(SO_4K)_2,6H_2O$.
(iv) SYLVINE or potassium chloride, KCl.
(v) BISCHOFITE or magnesium chloride, $MgCl_2,6H_2O$.

In the natural evaporation of sea-water, which has led to the formation of ROCK-SALT, the conditions prevailing have been different from those used in the laboratory, mainly on account of the inflow of normal sea-water, either constantly to replace water lost by evaporation or periodically. Under these conditions, the character of the deposit is modified profoundly; thus, at all temperatures above 30° calcium sulphate is precipitated from a solution saturated with common salt in the form of ANHYDRITE, $CaSO_4$, instead of as

gypsum, $CaSO_4,2H_2O$; and when other salts are present this temperature is lowered to 25°. When magnesium and potassium salts have accumulated in the liquor, the calcium sulphate is thrown down with the sulphates of these elements as POLYHALITE, $2CaSO_4,Mg(SO_4K)_2,H_2O$. Again, magnesium sulphate, which separates from water as EPSOMITE, $MgSO_4,7H_2O$, crystallises from solutions saturated with salt and rich in magnesium chloride, as KIESERITE, $MgSO_4,H_2O$, a mineral which is almost insoluble in water. Many minerals may thus appear in the salt beds which cannot be recrystallised from water but are stable in contact with solutions already saturated with common salt.

In this process of concentration the potassium and magnesium salts accumulate in the mother liquor with the bromides, borates, and other minor constituents of sea-water. In some localities these mother liquors have been evaporated to dryness and preserved from deliquescence and re-solution by impermeable deposits of clay, giving rise to deposits of KIESERITE, $MgSO_4,H_2O$, and CARNALLITE, $KMgCl_3,6H_2O$, above the main deposits of gypsum, salt, anhydrite, and polyhalite, as at Stassfurt, near Magdeburg, in Germany, and in Alsace. More usually, the salt beds contain only common salt, alternating with zones of anhydrite, or with clay and other sedimentary deposits ; thus, in the main salt-zone at Stassfurt, layers of salt 8 to 9 cm. in thickness alternate with bands of anhydrite about 7 mm. in thickness ; the maximum thickness of the beds is more than half a mile, corresponding with about 10,000 of these annual (?) deposits, and the volume of sea-water evaporated represents a total depth of 30 miles.

The largest salt mines in the world are at Wielitzka, in Galicia, where the deposits are said to be 500 miles long, 20 miles broad, and 1200 feet thick. In this country important beds of rock-salt occur at Nantwich (Cheshire), Droitwich (Worcestershire), and Middlesborough (Durham), but much of this deposit is under water, and the salt is largely obtained in the form of brine and recovered by evaporation.

A typical rock salt from Cheshire contains about $1\frac{1}{2}$ per cent. of $CaSO_4$, and 1 per cent. of $MgCl_2$, whilst the brine pumped from the " brine wells " in Cheshire and Worcestershire contains

$$NaCl = 22 \text{ to } 25 \text{ per cent.}$$
$$CaSO_4 = 0{\cdot}4 \text{ per cent.}$$
$$Na_2SO_4 = 0{\cdot}2 \text{ to } 0{\cdot}4 \text{ per cent.}$$

The annual production of salt in all countries is about 15 million tons.

(*b*) *Extraction of Salt from Brine.*—The brine which is pumped up from the salt beds contains calcium and magnesium salts, which are usually removed before evaporating the solution. This can be effected by electrolysis, which sets free a small quantity of sodium hydroxide ; this is converted into carbonate by the carbon dioxide dissolved in the water, and then precipitates the calcium and magnesium as carbonates. The best quality of salt is made by purifying the brine by contact with barium carbonate, which removes the sulphate as well as the calcium and magnesium, *e.g.*,

$$CaSO_4 + BaCO_3 = CaCO_3 + BaSO_4.$$

The purified brine is boiled down in shallow iron pans made of boiler plate, about 30 feet long, 20 feet wide, and 15 to 18 inches deep. Rapid boiling produces small crystals, which are collected by a perforated "skimmer," thrown into wooden boxes, and dried in an oven. The fine-grained material obtained in this way forms BAR-SALT; if made from unpurified brine it contains 0·1 to 0·5 per cent. of magnesium chloride and is therefore slightly deliquescent. Slower evaporation at 60° to 80° produces a coarser and less pure salt, which is used for manufacturing purposes. FISH-SALT is a large-grained product used for salting fish and is obtained by slower evaporation at a lower temperature.

In some modern plants the evaporation is conducted in a MULTIPLE-EFFECT vacuum plant (Fig. 18, p. 20), in which vapour from one pan is used to evaporate liquid in the next by making use of a suitable gradation of pressures. The solution in the first pan is evaporated by "live" steam from the boiler. The steam escaping from it serves to boil the liquid in the second pan, in which the boiling-point is reduced from 107° to about 80° by maintaining a partial vacuum. The steam from the second pan evaporates the solution in the third pan, in which a higher vacuum is maintained so as to reduce the boiling-point to about 40° or 50°. This system results in a great economy of fuel and an increased production of fine-grained salt owing to the rapid evaporation of the brine under reduced pressure in a vacuum. Thus, in one case a fuel with an evaporative power of about 5 lb. of water per lb. of fuel in an ordinary plant was found to give an evaporation of 14½ lb. of water per lb. of fuel in a much smaller time when using a "triple-effect" plant.

(*c*) *Physical Properties of Salt.*—Sodium chloride crystallises in transparent, colourless cubes, of density 2·17, often arranged in the form of a hollow stepped-pyramid. It melts at 800° and vaporises at higher temperatures. The crystals are free from double refraction; they are also very transparent to infra-red radiations and are therefore used for making lenses and prisms.

(*d*) *Salt and Water.*—The solubility of sodium chloride is very nearly the same in hot water as in cold water, *e.g.*, 100 grams of a saturated solution contain 26·3 grams of NaCl at 0°, 28·1 grams of NaCl at 100°, and 31 grams of NaCl under pressure at 180° (Fig. 214). The sparing solubility of common salt at high temperatures is frequently used to bring about double decomposition (compare p. 202), *e.g.*, in converting sodium nitrate into potassium or calcium nitrate,

$$NaNO_3 + KCl = KNO_3 + NaCl,$$
$$2NaNO_3 + CaCl_2 = Ca(NO_3)_2 + 2NaCl;$$

after boiling down the mixed solution until most of the salt has separated, a little water is added to prevent any further separation of salt, and the nitrate is then crystallised out by cooling.

Since salt cannot be crystallised out in the usual way from a hot solution, pure sodium chloride for chemical purposes is prepared by passing hydrogen chloride gas into a saturated aqueous solution of salt; the salt, which is much less soluble in presence of its acid, is

thrown down in small crystals, and melted to free it completely from water and acid.

A solution of salt in water, containing 22·42 grams of NaCl in 100 grams of solution, freezes at − 21·2°, *i.e.*, at a lower temperature than any other mixture of these two compounds; such a mixture is called an EUTECTIC MIXTURE (Greek εὖ, well, τήκειν, to melt), and the temperature at which it solidifies is called the EUTECTIC TEMPERATURE (p. 182). The solid eutectic mixture of ice and salt approximates in composition to the imaginary "cryohydrate," $NaCl,10H_2O$, which requires 24·5 per cent. of NaCl, but is merely a mechanical mixture of crystals of ice and salt and not a chemical compound. Below 0°, however, the salt may crystallise as a **dihydrate**, $NaCl,2H_2O$, as indicated in the equilibrium diagram, Fig. 214.

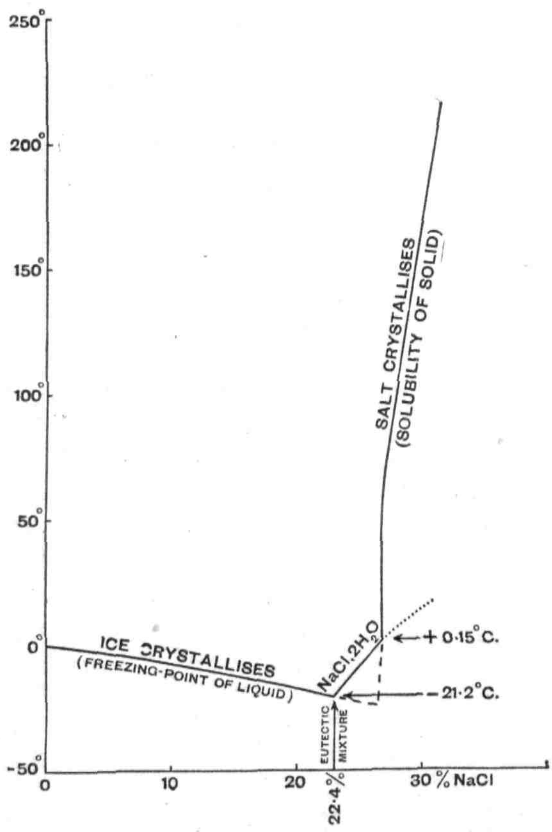


FIG. 214.—EQUILIBRIUM-DIAGRAM FOR SALT AND WATER.

(*d*) *Chemical Properties of Salt.*—Sodium chloride is decomposed by sulphuric acid and other strong acids, liberating hydrogen chloride gas. Even carbon dioxide liberates traces of hydrochloric acid from a cold solution of common salt, and develops a deep pink colour with methyl-orange and salt,

$$NaCl + H_2CO_3 \rightleftharpoons NaHCO_3 + HCl.$$

On passing carbon dioxide and ammonia into saturated brine, the ammonia combines with the hydrochloric acid shown in this equation and the action proceeds to a point at which sodium hydrogen carbonate is precipitated as in the Solvay process of making soda (p. 571).

On electrolysis, sodium chloride is decomposed into sodium and chlorine; this action can be used for the preparation of alkalies and bleach by keeping separate the products formed at the anode and cathode, or of hypochlorites, chlorates, and perchlorates by mixing them together.

(e) *Uses.*—Salt is the principal source of chlorine and sodium and of all their compounds which are prepared artificially; it is also used in glazing earthenware. It is an essential constituent of the food of man and other animals, and is largely manufactured for this purpose; it is also used for preserving fish, meat, and other foods.

Sodium Hypochlorite, NaOCl.

Sodium hypochlorite is formed when chlorine is passed into a cold solution of sodium hydroxide,

$$2NaOH + Cl_2 = NaCl + NaOCl + H_2O.$$

By cooling a concentrated solution, crystals of the composition $NaOCl,5H_2O$ can be prepared, which are more stable than the solution. Solutions containing sodium hypochlorite can also be made

(i) By decomposing bleaching powder by a solution of sodium carbonate, which gives solutions containing 7 to 15 per cent. of "available chlorine" (p. 635).

$$CaOCl_2 + Na_2CO_3 = CaCO_3 + NaCl + NaOCl.$$

(ii) By electrolysing sea-water or a dilute solution of sodium chloride (1 to 2 per cent.) at a temperature not exceeding 25°.

These solutions contain free hypochlorous acid and are extremely active bleaching agents. Solutions prepared from sea-water or stabilised by the addition of magnesium chloride are used extensively for disinfecting, *e.g.*, on hospital ships.

Sodium chlorate, $NaClO_3$, and **sodium perchlorate,** $NaClO_4$, closely resemble the corresponding potassium salts (p. 590), but are more soluble in water. Sodium chlorate, mixed with paraffin wax, has been used as an explosive, but is rather over-sensitive, as it can be fired by a blow between wooden surfaces.

Sodium bromide, NaBr, density 3·1, melting-point 765°, and **sodium iodide,** NaI, density 3·66, melting-point 660°, are analogous to the corresponding potassium salts (p. 590) and are used in medicine; sodium iodide differs from potassium iodide in being deliquescent in moist air.

Sodium and Oxygen. Manufacture of Soda.

Sodium Oxides.

(*a*) **Disodium monoxide,** Na_2O, is formed when a limited supply of oxygen is passed over sodium at a temperature below 180°. It dissolves violently in water, forming sodium hydroxide,

$$Na_2O + H_2O = 2NaOH.$$

(*b*) **Disodium dioxide** or **sodium peroxide,** Na_2O_2, is manufactured by heating metallic sodium in aluminium trays in an excess of dry air free from carbon dioxide; the product, which contains about 93 per cent. of Na_2O_2, is yellow, but on absorbing water and carbon dioxide from the air it becomes white. It is a powerful oxidising agent, carbonising and frequently igniting organic substances such as wood or paper with which it comes in contact; when added to glacial acetic acid, the whole mass bursts into flame. It absorbs carbon dioxide, forming sodium carbonate and liberating oxygen; it also absorbs carbon monoxide according to the equation

$$Na_2O_2 + CO = Na_2CO_3.$$

When the solution in cold water is evaporated, hexagonal crystals of the **octahydrate,** $Na_2O_2,8H_2O$ separate; the same hydrate is formed by adding alcohol to a solution of sodium hydroxide in aqueous hydrogen peroxide. On boiling a solution of sodium peroxide it loses oxygen and forms sodium hydroxide. These facts show that the action

$$Na_2O_2 + 2H_2O \rightleftharpoons 2NaOH + H_2O_2$$

is reversible. A solution of sodium peroxide in hydrochloric acid (containing sodium chloride and hydrogen peroxide) is used for bleaching. The peroxide is also used as an oxidising agent in the analysis of minerals such as iron pyrites and chrome ironstone.

Sodium hydroxide or **caustic soda,** NaOH.

(*a*) *Manufacture from Carbonate.*—Until recently, caustic soda was manufactured almost exclusively by "causticising" sodium carbonate by boiling a 10 per cent. solution of the carbonate with lime in iron vessels,

$$Ca(OH)_2 + Na_2CO_3 \rightleftharpoons CaCO_3 + 2NaOH.$$

Stronger solutions give a diminished yield of sodium hydroxide, since the action is reversible and concentrated sodium hydroxide will reconvert chalk into lime. The solution is filtered and concentrated by evaporation, during which impurities such as sodium sulphate and carbonate separate and are removed by decantation, or, in the later stages, by ladling; the syrup is finally purified by blowing air through it, or by adding a little sodium nitrate to oxidise sulphides and cyanogen compounds, and is then cast in iron drums. This method of manufacture is specially adapted to working up the sodium carbonate contained in the mother liquors of the Leblanc process (p. 569).

The dry sodium carbonate prepared by the Solvay process (p. 571) can be causticised by heating with ferric oxide in rotating cylinders, whereby sodium ferrite, $NaFeO_2$, is formed,

$$Na_2CO_3 + Fe_2O_3 = CO_2 + 2NaFeO_2;$$

the product is extracted with a minimum of hot water, giving a concen-

trated solution of sodium hydroxide, whilst the insoluble ferric oxide is regenerated,

$$2NaFeO_2 + H_2O = 2NaOH + Fe_2O_3.$$

(*b*) *Manufacture by Electrolysis.*—Many processes have been introduced during recent years for the manufacture of sodium hydroxide (or sodium carbonate) directly from salt by electrolysis. The essential actions are :

$$NaCl = \overset{+}{Na} + \overset{-}{Cl}; \quad 2Na + 2H_2O = 2NaOH + H_2.$$

Sodium hydroxide and hydrogen are produced at the cathode, and chlorine at the anode ; it is therefore very important to keep these products separate, in order to prevent the formation of hypochlorites and chlorates or of explosive mixtures of hydrogen and chlorine. Three methods of working may be distinguished :

(i) Electrolysis of salt solution without diaphragms,
(ii) Electrolysis of salt solution with diaphragms,
(iii) Electrolysis of fused sodium chloride.

(i) *Without Diaphragms.*—In the CASTNER-KELLNER PROCESS as represented diagrammatically in Fig. 215, the electrolytic bath is divided into three parts by partitions dipping into a layer of mercury which acts as a seal to separate the contents of the three compartments. The lateral compartments contain carbon anodes in contact with the brine which is to be electrolysed, whilst the central compartment contains an iron cathode in contact with water or an aqueous solution of sodium hydroxide. The mercury, acting as an intermediate electrode, serves as a cathode in the outer compartments and as an anode in the inner compartment, and is made to flow backwards and forwards by an eccentric which causes one end of the bath to rise and fall. Chlorine is liberated at the carbon anodes in the outer compartments, and is conveyed away in pipes to be converted into bleaching powder, carbon tetrachloride, or other products, whilst the mercury (acting here as a cathode) absorbs the sodium in the form of sodium amalgam and protects it from decomposition by the water in the brine. In the central compartment, caustic soda is electrolysed,

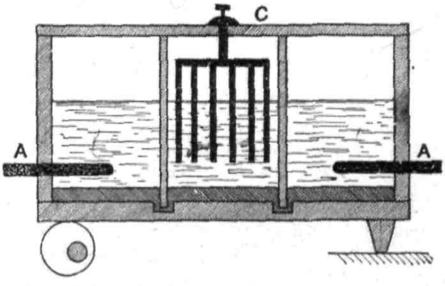


FIG. 215.—DIAGRAMMATIC REPRESENTATION OF CASTNER-KELLNER PROCESS.

$$NaOH = \overset{+}{Na} + \overset{-}{OH};$$

the sodium amalgam is attacked by the hydroxyl ions, forming sodium hydroxide, and regenerating pure mercury; at the same time an equivalent quantity of sodium is set free at the iron cathode and converted into sodium hydroxide and hydrogen by the action of water upon it.

(ii) *With Diaphragms.*—Several different forms of apparatus have been devised in which the alkali set free at the cathode and the chlorine set free at the anode are kept apart by means of a porous partition or diaphragm. It is essential that the diaphragm shall not offer too great a resistance to the current, but it must not allow the contents of the anode and cathode compartments to diffuse or to flow into one another, nor must the diaphragm be attacked by the alkali or by the chlorine.

In some of these plants, the anode consists of carbon rods. In other cases, magnetic oxide of iron, prepared by fusing ferric oxide at the temperature of the electric arc, is cast into rods and used as the anode; these rods are good conductors and have the advantage that they are not attacked by oxygen or by chlorine, whereas carbon anodes are oxidised to carbon dioxide whenever oxygen is produced during the electrolysis. The cathodes are generally constructed from iron rods. The diaphragm may be in the form of a bag, or of flat sheets, consisting largely of asbestos. In the BILLITER PROCESS (Fig. 216), purified brine is allowed to soak through a horizontal partition *D* at the bottom of the anode compartment, in which chlorine is set free at the graphite anodes *AAA* and is driven out from the solution with the help of steam coils *SS*, whilst sodium hydroxide and hydrogen are formed at a cathode of wire gauze in contact with the lower surface of the partition. The space *R* below the partition is empty, and any excessive flow of brine into it is checked by adding barium sulphate to the liquid above the partition. Caustic soda is drawn off through a syphon *U*, and chlorine at *C*, whilst hydrogen escapes at *W*.

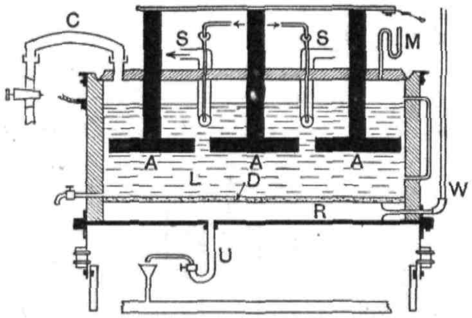


FIG. 216.—BILLITER CELL.

(iii) *Electrolysis of Fused Sodium Chloride.*—In the ACKER PROCESS, as developed at Niagara, molten salt is electrolysed between graphite anodes and a cathode of molten lead. The lead is caused to circulate by means of a jet of steam which acts upon the sodium (about 4 per cent.) dissolved in the lead, regenerating metallic lead and producing sodium hydroxide and hydrogen. The heat required to melt the salt

and to keep the lead molten is produced by the electric current. This process has the advantage that anhydrous sodium hydroxide can be produced and the costly process of evaporating the aqueous liquor is eliminated.

Purification of Sodium Hydroxide.

Sodium hydroxide may be purified by dissolving it in alcohol, in which the chloride, carbonate, and sulphate are only sparingly soluble, and evaporating the solution in a silver dish; the product is known as sodium hydroxide "pure by alcohol."

Sodium hydroxide free from non-metallic impurities was formerly prepared by the action of water or of water vapour upon metallic sodium, and sold as "pure, from metal"; but as the sodium hydroxide prepared by the Castner-Kellner process is actually made from sodium amalgam, this method of preparation is no longer needed, unless complete freedom from carbonates is required.

Properties and Uses of Sodium Hydroxide.

(*a*) *Physical Properties.*—Sodium hydroxide forms milky-white, crystalline lumps or powder; in the laboratory, it is generally used in the form of sticks cast from the melted solid. It undergoes a change of crystalline form at 300° and melts at 318°, the corresponding temperatures for potassium hydroxide being 248° and 360°; each form of sodium hydroxide is isomorphous with the corresponding form of potassium hydroxide, but the freezing-point curve droops to 185°, and the transition-point curve to 180° at about 40 mols. per cent. of potassium hydroxide (Fig. 217). The solid is very deliquescent; it dissolves in an equal weight of water at the ordinary temperature and, unlike most salts, remains molten instead of crystallising out when the solution is concentrated. When it is dissolved in water there is a great evolution of heat,

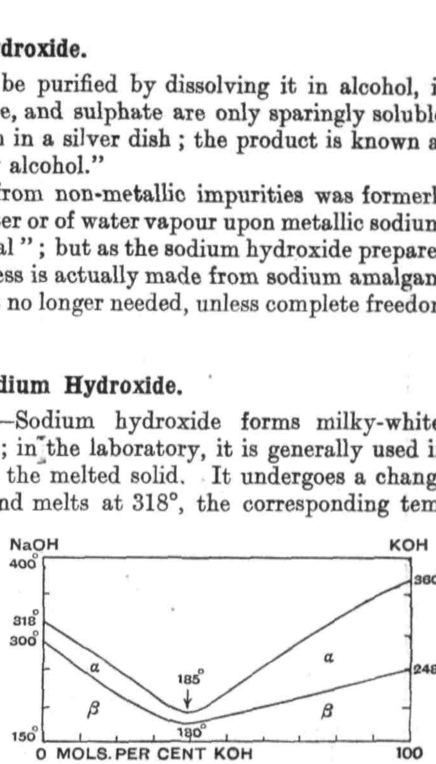


FIG. 217.—FREEZING-POINTS AND TRANSITION-TEMPERATURES OF SODIUM AND POTASSIUM HYDROXIDES.

$$NaOH + Aq = NaOH,Aq + 10{,}000 \text{ calories,}$$

and the contraction which takes place is so large that 14 grams of the hydroxide can be dissolved in 86 grams of water without increasing its volume, the "solution volume" (p. 250) of sodium hydroxide being negative over this range of concentrations.

(*b*) *Chemical Properties.*—Sodium hydroxide is a powerful alkali

with a strong caustic action upon the skin. It neutralises acids forming sodium salts, and is converted by carbon dioxide into sodium carbonate and bicarbonate,

$$2NaOH + CO_2 = Na_2CO_3 + H_2O; \quad NaOH + CO_2 = NaHCO_3.$$

It liberates ammonia from ammonium salts, and precipitates insoluble oxides or hydroxides from aqueous solutions of metallic salts, *e.g.*,

$$NH_4Cl + NaOH = NaCl + NH_3 + H_2O$$
$$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4;$$

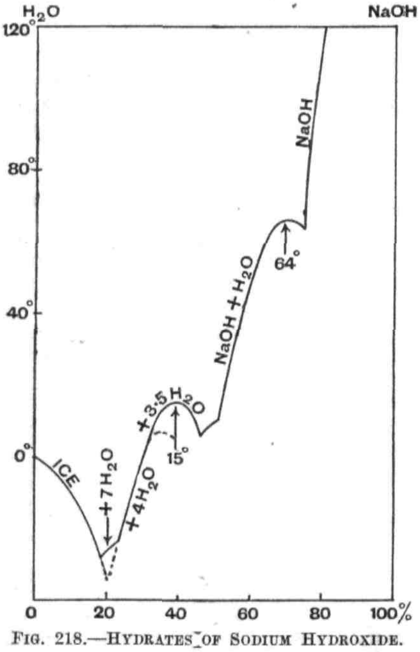


FIG. 218.—HYDRATES OF SODIUM HYDROXIDE.

some of these hydroxides which possess slight acidic properties are dissolved by an excess of the alkali, *e.g.*,

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$$
$$NaOH + Al(OH)_3 = NaAlO_2 + 2H_2O.$$

When boiled with fats it converts them into hard soap, and even in the cold it has the property of emulsifying oils and grease, thus acting as a cleansing agent in removing greasy dirt. The hydroxide is a very stable compound and cannot be converted directly into the oxide, but when heated strongly with carbon it gives sodium, hydrogen, and carbon monoxide,

$$2NaOH + 2C = 2Na + H_2 + 2CO.$$

(*c*) *Hydrates.*—The most important hydrates of sodium hydroxide (Fig. 218, compare potassium hydroxide, Fig. 222, p. 594) are:

Hydrate.	*Melting-point.*
$2NaOH,7H_2O$	15·5°
$NaOH,2H_2O$	12·3 (giving the monohydrate and water)
$NaOH,H_2O$	64·3

Hydrates containing 3, 4, 5, and $7H_2O$ have also been described.

(*d*) *Uses.*—Caustic soda is employed principally in the manufacture of soap; it is also used in paper-making, in the bleaching of cotton and linen, and in many chemical industries.

Sodium Carbonate, Na_2CO_3.

(*a*) *Occurrence.*—NATIVE SODA (p. 47) is found in the SODA LAKES of Egypt, and in the desert regions of Lake Magadi in East Africa, in the form of TRONA or **sodium sesquicarbonate**, $Na_2CO_3,NaHCO_3,2H_2O$. **Sodium carbonate**, Na_2CO_3, is found in the ashes of sea-plants, which yield soda where land-plants yield potash. The **decahydrate**, $Na_2CO_3,10H_2O$, is known as WASHING SODA.

(*b*) *Manufacture.*—Sodium carbonate was formerly prepared under the name of BARILLA from the ashes of sea-plants, but is now manufactured from common salt:

(i) By the Leblanc Process;
(ii) By the Ammonia-soda or Solvay Process.

The electrolytic process can also be modified to produce sodium carbonate instead of sodium hydroxide, but as the latter product is more valuable, the change is not usually advantageous.

Manufacture of Soda by the Leblanc Process.

When the supplies of foreign soda were cut off from France during the wars which followed the French Revolution, the manufacture of soda from salt became so urgent that the Government offered a prize for the discovery of a suitable method. The successful process is known as the LEBLANC PROCESS and remained in use for more than a century. It was carried out in two stages, namely, the SALT-CAKE PROCESS, in which sodium chloride is converted into sodium sulphate, and the BLACK-ASH PROCESS, in which sodium sulphate is converted, through the sulphide, into sodium carbonate.

(*a*) *Salt-cake Process.*—Common salt (16 cwt.) is placed in a semicircular iron pan, heated by flue gases from a furnace, and chamber acid (1800 lb. of density 1·42) is added in sufficient quantity to convert the sodium chloride completely into sulphate,

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4.$$

One molecule of salt is decomposed rapidly by the sulphuric acid, converting it into sodium hydrogen sulphate,

$$NaCl + H_2SO_4 = NaHSO_4 + HCl,$$

and liberating large volumes of hydrogen chloride gas, which pass out of a central opening above the pan, and are converted into hydrochloric acid by absorption with water in condensing towers.

In order to decompose the second molecule of salt, the product is raked on to the hearth of a furnace, which should be of the closed or muffle type in order to avoid dilution of the hydrogen chloride with flue gases, and contamination by soot; it is there heated to a higher temperature in order to bring about the decomposition shown in the equation

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

The product is known as SALT-CAKE.

with a strong caustic action upon the skin. It neutralises acids forming sodium salts, and is converted by carbon dioxide into sodium carbonate and bicarbonate,

$$2NaOH + CO_2 = Na_2CO_3 + H_2O; \quad NaOH + CO_2 = NaHCO_3.$$

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$$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4;$$

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When boiled with fats it converts them into hard soap, and even in the cold it has the property of emulsifying oils and grease, thus acting as a cleansing agent in removing greasy dirt. The hydroxide is a very stable compound and cannot be converted directly into the oxide, but when heated strongly with carbon it gives sodium, hydrogen, and carbon monoxide,

$$2NaOH + 2C = 2Na + H_2 + 2CO.$$

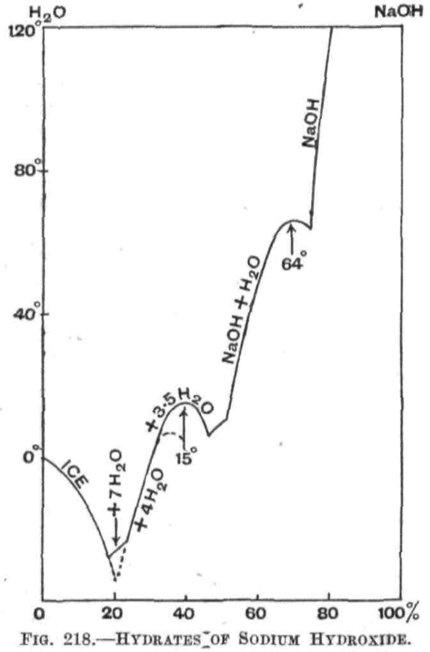


FIG. 218.—HYDRATES OF SODIUM HYDROXIDE.

(c) *Hydrates.*—The most important hydrates of sodium hydroxide (Fig. 218, compare potassium hydroxide, Fig. 222, p. 594) are :

Hydrate.	*Melting-point.*
$2NaOH,7H_2O$	15·5°
$NaOH,2H_2O$	12·3 (giving the monohydrate and water)
$NaOH,H_2O$	64·3

Hydrates containing 3, 4, 5, and $7H_2O$ have also been described.

(*d*) *Uses.*—Caustic soda is employed principally in the manufacture of soap ; it is also used in paper-making, in the bleaching of cotton and linen, and in many chemical industries.

Sodium Carbonate, Na_2CO_3.

(*a*) *Occurrence.*—NATIVE SODA (p. 47) is found in the SODA LAKES of Egypt, and in the desert regions of Lake Magadi in East Africa, in the form of TRONA or **sodium sesquicarbonate,** $Na_2CO_3,NaHCO_3,2H_2O$. **Sodium carbonate,** Na_2CO_3, is found in the ashes of sea-plants, which yield soda where land-plants yield potash. The **decahydrate,** $Na_2CO_3,10H_2O$, is known as WASHING SODA.

(*b*) *Manufacture.*—Sodium carbonate was formerly prepared under the name of BARILLA from the ashes of sea-plants, but is now manufactured from common salt:

(i) By the Leblanc Process;
(ii) By the Ammonia-soda or Solvay Process.

The electrolytic process can also be modified to produce sodium carbonate instead of sodium hydroxide, but as the latter product is more valuable, the change is not usually advantageous.

Manufacture of Soda by the Leblanc Process.

When the supplies of foreign soda were cut off from France during the wars which followed the French Revolution, the manufacture of soda from salt became so urgent that the Government offered a prize for the discovery of a suitable method. The successful process is known as the LEBLANC PROCESS and remained in use for more than a century. It was carried out in two stages, namely, the SALT-CAKE PROCESS, in which sodium chloride is converted into sodium sulphate, and the BLACK-ASH PROCESS, in which sodium sulphate is converted, through the sulphide, into sodium carbonate.

(*a*) *Salt-cake Process.*—Common salt (16 cwt.) is placed in a semicircular iron pan, heated by flue gases from a furnace, and chamber acid (1800 lb. of density 1·42) is added in sufficient quantity to convert the sodium chloride completely into sulphate,

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4.$$

One molecule of salt is decomposed rapidly by the sulphuric acid, converting it into sodium hydrogen sulphate,

$$NaCl + H_2SO_4 = NaHSO_4 + HCl,$$

and liberating large volumes of hydrogen chloride gas, which pass out of a central opening above the pan, and are converted into hydrochloric acid by absorption with water in condensing towers.

In order to decompose the second molecule of salt, the product is raked on to the hearth of a furnace, which should be of the closed or muffle type in order to avoid dilution of the hydrogen chloride with flue gases, and contamination by soot; it is there heated to a higher temperature in order to bring about the decomposition shown in the equation

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

The product is known as SALT-CAKE.

(*b*) ***Black-ash Process.***—The salt-cake is mixed with limestone and powdered coal and heated to 700–1000°, either in a special reverberatory furnace termed a BALLING FURNACE, or in a ROTARY FURNACE consisting of a slowly revolving cylinder 18 to 25 feet long and 8 to 12 feet in diameter lined with firebricks and heated by hot gases passing up the centre of the cylinder. The use of a rotary furnace results in a great economy of manual labour and ensures a more rapid action and a more uniform product, from which also the carbonate can be extracted more easily. The waste gases from the furnace can be used to concentrate the solution of sodium carbonate which is produced in the next stage of the process. The following changes take place :

$$\text{(i)}\ Na_2SO_4 + 2C = Na_2S + 2CO_2.$$
$$\text{(ii)}\ Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The end of the operation is shown by the appearance of yellow flames on the surface of the mass, due to the production of carbon monoxide (coloured yellow by sodium) by the action,

$$CaCO_3 + C = CaO + 2CO.$$

It is important that the coal used should contain as little ash as possible, especially silica, which would interact with the carbonate to form sodium silicate, Na_2SiO_3 ; it must also contain little nitrogen, so as not to form cyanides and sulphocyanides. The product is known as BLACK ASH.

Salt-cake contains about 95 per cent. of Na_2SO_4, 1·5 per cent. of $NaHSO_4$, and 1·3 per cent. of NaCl. The black-ash prepared from it contains about 35 to 45 per cent. of Na_2CO_3, 0·5 to 1·5 per cent. of Na_2SO_4, 1·5 to 2·5 per cent. of NaCl, and 28 to 31 per cent. of CaS, together with variable quantities of lime (8 to 10 per cent.), calcium carbonate (3 to 6 per cent.), coal, and other impurities in smaller proportion.

(*c*) *Lixiviation of Black-ash.*—The porous lumps of black-ash are extracted with water in such a way as to dissolve a maximum quantity of soda in a minimum quantity of water. This process of extraction with water is described as LIXIVIATION. The residue consists mainly of calcium sulphide, lime, and calcium carbonate and forms the so-called ALKALI WASTE. It contains all the sulphur present in the sulphuric acid used in the first stage of the process, and was formerly a troublesome by-product. It can be worked up, however, by the Chance-Claus SULPHUR-RECOVERY PROCESS, as shown in the equations

$$2CaS + 3O_2 = 2CaSO_3$$
$$2CaS + CaSO_3 + 3CO_2 = 3CaCO_3 + 3S,$$

and made to regenerate much of the sulphur which it contains ; it can also be used to make thiosulphates (p. 638) ; in this way a very objectionable by-product is converted into a source of profit.

(*d*) *Crystallisation.*—The TANK-LIQUOR from the lixiviation contains about 25 per cent. of soda, a part of which is in the caustic form on account of the presence of free lime in the black-ash. In order to recon-

vert the sodium hydroxide into carbonate, the solution is caused to trickle down towers, containing broken stoneware, up which furnace gases containing carbon dioxide are led. It is then evaporated in tanks heated by waste gases from the black-ash furnace. Evaporation at the boiling-point gives BLACK SALT, a crude and impure monohydrate, Na_2CO_3,H_2O, contaminated by coal-dust and other impurities. This is calcined in a reverberatory furnace in order to burn out the impurities, and is then known as SODA-ASH, or REFINED ALKALI; this may contain 98–99 per cent. of Na_2CO_3, but the lower grades may contain 3–4 per cent. of NaOH, 5 per cent. of Na_2SO_4, and 2–3 per cent. of NaCl.

WASHING SODA, $Na_2CO_3,10H_2O$, is prepared by saturating an aqueous solution with the carbonate at about 35° (the temperature of maximum solubility) and allowing it to crystallise on cooling; it is the form generally sold for household use, but contains only 37 per cent. of Na_2CO_3, even when pure, the remaining 63 per cent. of the crystals consisting of water. CRYSTAL CARBONATE, Na_2CO_3,H_2O, is obtained by evaporation at the boiling-point; it contains a much higher proportion of the carbonate than washing soda, and is therefore much more economical, especially when the cost of freight has to be considered.

(*e*) *Review of the Leblanc Process.*—The principal disadvantages of the Leblanc process are (i) the employment of rock-salt instead of brine; this cost 12*s.* per ton at a time when salt in the form of brine cost about 3*d.* per ton; (ii) the use of a costly raw material, namely, sulphuric acid, which is converted into a waste product (alkali waste) from which only a part of the sulphur can be recovered. Its special advantage is that it affords valuable by-products, including sulphur-compounds, such as calcium sulphide and thiosulphate (p. 638), and hydrochloric acid, which finds employment in the manufacture of chlorine, bleaching powder, chlorates, and in many industries. Had it not been for this, it is probable that the Leblanc process would have been superseded long ago by the Solvay process or by the electrolytic process described below; indeed, the Leblanc process was sometimes worked through its first stage only, since sodium sulphate (unlike sodium chloride) can be used in glass-manufacture without converting it into carbonate.

Solvay Process or Ammonia Soda Process.

The AMMONIA-SODA PROCESS, although patented as early as 1838, only became of industrial importance after 1865, when improvements introduced by Solvay of Brussels made it technically successful. It is based on the fact that when carbon dioxide is passed into a solution of common salt containing ammonia, ammonium chloride is formed and sodium bicarbonate precipitated,

$$NaCl + NH_3 + H_2O + CO_2 = NaHCO_3 + NH_4Cl. \qquad \text{(i)}$$

The process depends for its success on the slight solubility of sodium

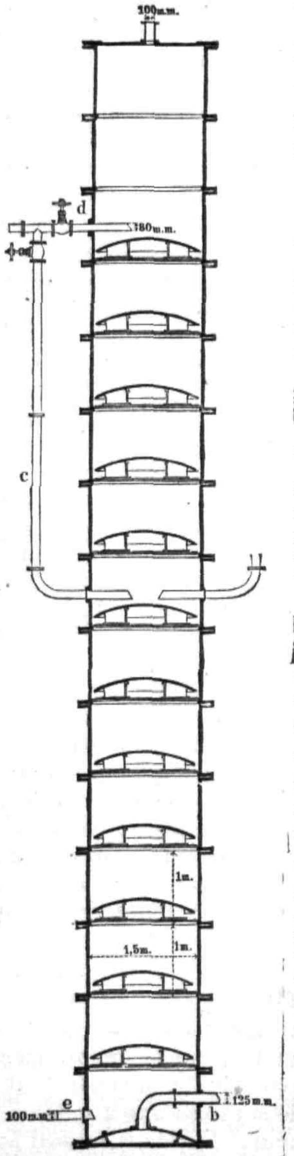


FIG. 219.—SOLVAY TOWER.

bicarbonate, which causes it to separate as a crystalline powder, which can readily be filtered off, washed, and drained. When heated, the bicarbonate loses carbon dioxide, which supplies one-half of that required by equation (i) above,

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2 . \quad . \quad . \quad (ii)$$

The solution of ammonium chloride left after the separation of the sodium bicarbonate is heated with slaked lime, which regenerates the ammonia almost without loss,

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O . \quad . \quad (iii)$$

The lime required to decompose the ammonium chloride in equation *(iii)* and the balance of the carbon dioxide required in equation (i) are obtained by heating limestone (Fig. 177, p. 456),

$$CaCO_3 = CaO + CO_2 . \quad . \quad . \quad . \quad (iv)$$

The economical success of the process depends on the recovery of the ammonia, which with careful working is so complete that in practice the only materials used up are common salt and chalk; moreover, the salt can be used in the form of brine, at little more than the cost of pumping. The cost of raw materials is therefore very small, and the plant and methods of working have been developed until the yield from a single tower may amount to 200 tons per day. The whole of the chlorine of the salt is lost in the form of calcium chloride, for which no satisfactory use has yet been found; this disadvantage will, however, disappear when the Solvay process is worked in conjunction with the Haber process (p. 378), in order to convert synthetic ammonia into ammonium chloride for use as a fertiliser, in place of ammonium sulphate, thus eliminating the sulphuric acid which is now generally used to absorb ammonia. The principal stages in the Solvay process are as follows:

(i) *Saturation.*—In the first stage of the process the brine is saturated with ammonia gas in a tower fitted with numerous partitions, down which the brine runs, in counter-current to the ammonia gas, which is pumped into the tower at its base. In this way the brine is saturated as completely as possible with fresh ammonia at the base of the tower whilst the last traces of ammonia are absorbed by fresh brine at the top of the tower.

(ii) *Carbonation.*—The carbonation is effected in a Solvay tower (Fig. 219), consisting of a large number of superposed cylindrical compartments or drums. The bottom of each compartment has a large circular hole covered with a perforated sieve, the object of which is to break up the carbon dioxide into small bubbles and so to obtain as perfect absorption as possible. The carbon dioxide is pumped in at the bottom of the towers, whilst the ammoniacal brine is admitted at the top in such a way as to fill the tower almost completely. The absorption of carbon dioxide by the ammoniacal solution, forming ammonium carbonate, $(NH_4)_2CO_3$, and then ammonium bicarbonate, $(NH_4)HCO_3$, liberates considerable heat, which is removed by a cold-water coil in each section. During the action the temperature is kept at 30–40°, but when nearing completion the temperature is reduced to about 15°, so as to bring about a maximum separation of sodium bicarbonate.

(iii) *Filtration.*—The pasty mass obtained from the bottom of the tower is passed on to vacuum filters, which retain the solid sodium bicarbonate. This is washed with a little water to remove mother liquor, dried, and decomposed by heating in iron pans, in such a way that the carbon dioxide generated can be used again. The sodium carbonate formed by igniting the bicarbonate in this process contains 98–99 per cent. of Na_2CO_3.

Properties of Sodium Carbonate.

(*a*) *Physical Properties.*—Anhydrous sodium carbonate, Na_2CO_3, is a white powder which melts at 850°; the melting-point is lowered when it is mixed with potassium carbonate, and the product is known as FUSION MIXTURE. It dissolves readily in water and forms a series of hydrates which are described below; its solubility at different temperatures is shown in Fig. 220 (*a*).

(*b*) *Hydrates of Sodium Carbonate.*—The principal hydrates are set out in the following table:

TABLE 69.—HYDRATES OF SODIUM CARBONATE.

Formula of hydrate.	*Name of hydrate.*	*Commercial name.*	*Range of stability.*
Na_2CO_3	—	Soda-ash	—
Na_2CO_3,H_2O	Monohydrate	Crystal Carbonate	above 35·4°
$Na_2CO_3,7H_2O$	Heptahydrate	—	32·0° to 35·4°
$Na_2CO_3,10H_2O$	Decahydrate	Washing Soda or Soda Crystals	2·1° to 32·0°

The various hydrates are stable in contact with water within the ranges of temperature shown in the table. Thus on boiling down a saturated solution of sodium carbonate the monohydrate separates continuously, whilst the decahydrate is formed when a hot concentrated solution is allowed to crystallise below 32°.

The anhydrous salt absorbs water from the air and forms the **monohydrate**, Na_2CO_3,H_2O, and this salt is also formed when the **decahydrate**, $Na_2CO_3,10H_2O$, is exposed to dry air; the loss of water is accompanied by EFFLORESCENCE (p. 252), *i.e.*, by the crumbling of the crystals of the decahydrate. These phenomena depend on the fact that the vapour pressure of the monohydrate is less, whilst the vapour

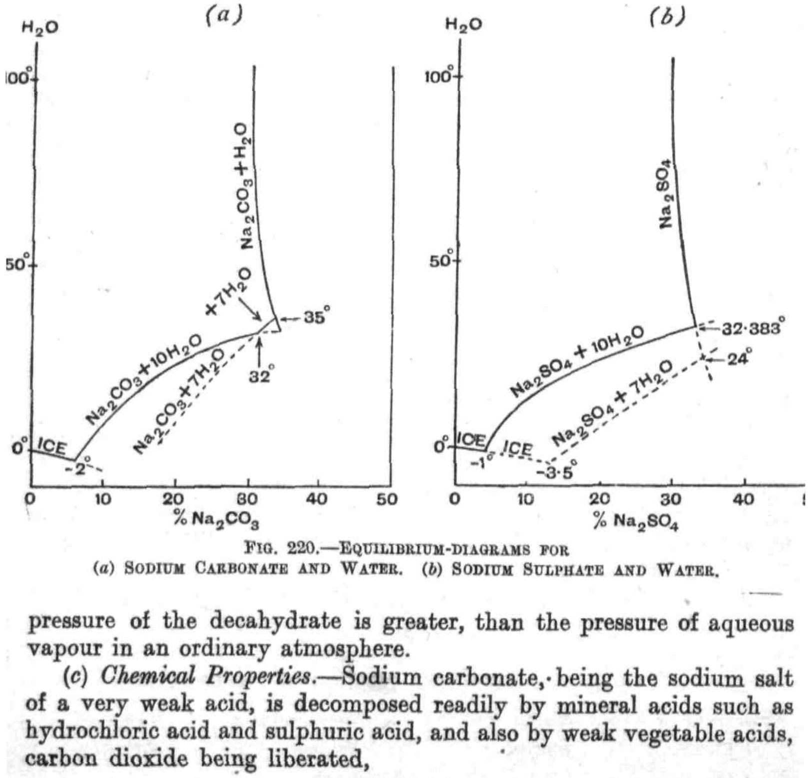


FIG. 220.—EQUILIBRIUM-DIAGRAMS FOR (*a*) SODIUM CARBONATE AND WATER. (*b*) SODIUM SULPHATE AND WATER.

pressure of the decahydrate is greater, than the pressure of aqueous vapour in an ordinary atmosphere.

(*c*) *Chemical Properties.*—Sodium carbonate, being the sodium salt of a very weak acid, is decomposed readily by mineral acids such as hydrochloric acid and sulphuric acid, and also by weak vegetable acids, carbon dioxide being liberated,

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O.$$

Aqueous solutions of sodium carbonate are alkaline and have an alkaline taste. The alkalinity is probably due to hydrolytic dissociation into sodium hydroxide and sodium bicarbonate, thus,

$$Na_2CO_3 + H_2O \rightleftharpoons NaOH + NaHCO_3,$$

an equilibrium between all four substances existing in the solution. This property is shared by other sodium salts of weak acids, which are also used as cleansing agents, *e.g.*, borax (sodium borate) and soap (sodium stearate or palmitate).

A solution of sodium carbonate absorbs carbon dioxide, forming the bicarbonate, $NaHCO_3$,

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3.$$

This absorption takes place most readily at a temperature of about 50°. When the temperature is raised to the boiling-point, the bicarbonate is decomposed slowly in the sense of the equation

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O,$$

carbon dioxide being evolved. On these facts is based an industrial process by which carbon dioxide can be manufactured on a large scale for liquefaction in steel cylinders. Coke is burnt, with a minimum supply of air, so that the products of combustion contain from 16 to 18 per cent. of CO_2, the remainder being mainly nitrogen; the carbon dioxide is absorbed from the flue gases by means of a dilute solution of sodium carbonate at about 50°, and regenerated in a pure state from the solution by boiling it.

(*d*) *Uses.*—Sodium carbonate is used in the manufacture of glass, as a cleansing agent for domestic purposes, in the working and bleaching of textile fibres, and for the preparation of other sodium salts (borax, sodium phosphate, etc.).

Sodium Bicarbonate (Sodium Hydrogen Carbonate), $NaHCO_3$.

When carbon dioxide is passed through a saturated solution of washing soda, sodium bicarbonate is precipitated as an anhydrous crystalline powder, owing to the fact that it is much less soluble in water than the carbonate. Thus, a solution saturated at 30° contains only 10 per cent. of the bicarbonate, whereas the carbonate dissolves to the extent of 29 per cent. of the weight of the solution. Solid sodium carbonate also absorbs moist gaseous carbon dioxide to form the bicarbonate,

$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3.$$

On a commercial scale, the bicarbonate is produced from salt in very large quantities as an intermediate product in the ammonia-soda process for making sodium carbonate (p. 571).

Solid sodium bicarbonate begins to decompose below 100°, giving off carbon dioxide; by heating rather more strongly, for example, over a Bunsen flame at 250–300°, anhydrous sodium carbonate is obtained. This method of preparing pure dry sodium carbonate is commonly used in analysis when making up standard solutions of this alkali; but if the heating is too intense, traces of caustic alkali may be formed.

Sodium bicarbonate is used in medicine and in the washing and bleaching of silk and wool.

Sodium Sesquicarbonate.

When a solution of sodium bicarbonate is boiled, sodium **sesquicarbonate**, $Na_2CO_3,NaHCO_3,2H_2O$, separates on cooling. This salt, which as a natural product is known as TRONA, is now sold under the name of BATH SALTS as a "mild" alkali for softening water; it is also used in wool-washing.

SODIUM AND SULPHUR.

Sodium Salts containing Sulphur.

These include:

(i) Salts containing *one* atom of sulphur in the molecule such as:

Sodium sulphide, Na_2S	Sodium hydrosulphide, NaHS
Sodium sulphite, Na_2SO_3	Sodium bisulphite, $NaHSO_3$
Sodium sulphate, Na_2SO_4	Sodium bisulphate, $NaHSO_4$.

(ii) Salts of the series $Na_2S_2O_x$, in which two atoms of sodium are united with *two* atoms of sulphur and various proportions of oxygen, *e.g.*,

Sodium disulphide,	Na_2S_2
Sodium thiosulphate,	$Na_2S_2O_3$
Sodium hydrosulphite,	$Na_2S_2O_4$
Sodium metabisulphite,	$Na_2S_2O_5$
Sodium dithionate,	$Na_2S_2O_6$
Sodium pyrosulphate,	$Na_2S_2O_7$
Sodium persulphate,	$Na_2S_2O_8$.

(iii) Salts of the formula $Na_2S_xO_6$, of which the most important is
Sodium tetrathionate, $Na_2S_4O_6$.

Sodium Sulphides and Polysulphides.

Sodium hydrosulphide, NaHS, is formed when a solution of sodium hydroxide is saturated with hydrogen sulphide; on evaporating the solution in a current of hydrogen sulphide, colourless, deliquescent crystals of the **dihydrate**, $NaHS,2H_2O$, are obtained.

Sodium sulphide, Na_2S, is formed when an equivalent quantity of sodium hydroxide is added to a solution of the hydrosulphide; on concentrating the solution, colourless crystals of the **enneahydrate**, $Na_2S,9H_2O$, separate. This salt is used extensively in the textile industries, in the manufacture of dyes and in the extraction of silver. It is manufactured by heating the sulphate with coal at about 1000°,

$$Na_2SO_4 + 2C = Na_2S + 2CO_2.$$

The mass is extracted with water and the solution evaporated so as to give crystals. The anhydrous sulphide, Na_2S, is also a commercial product.

Aqueous solutions of sodium sulphide are oxidised to sodium thiosulphate, $Na_2S_2O_3$, by exposure to air, small quantities of hydrogen sulphide being liberated at the same time by the action of carbonic acid.

A solution of sodium sulphide dissolves sulphur, forming a series of **sodium polysulphides**, Na_2S_n, of which the following have been obtained in a crystalline form:

$$Na_2S_2,5H_2O \qquad Na_2S_4,6H_2O \text{ and } Na_2S_4,8H_2O$$
$$Na_2S_3,3H_2O \qquad Na_2S_5,8H_2O.$$

Sodium Sulphite, Bisulphite, and Metabisulphite.

When a cold solution of sodium hydroxide is saturated with gaseous sulphur dioxide **sodium hydrogen sulphite** or **sodium bisulphite**, $NaHSO_3$, separates out as a crystalline powder smelling strongly of sulphur dioxide,

$$NaOH + SO_2 = NaHSO_3.$$

A solution of the salt is a commercial article, and is used to remove chlorine from vegetable tissues and fibres after bleaching, in the manufacture of paper, and for sterilising brewers' casks, etc. It can be precipitated from its solutions by alcohol, but when crystallised from water it loses water and gives **sodium metabisulphite**,

$$2NaHSO_3 = Na_2S_2O_5 + H_2O.$$

This form of the sulphite is prepared commercially by passing sulphur dioxide into dry "crystal carbonate," Na_2CO_3,H_2O, and is used in photography.

On adding one equivalent of sodium hydroxide (or sodium carbonate in the form of "soda-ash") to a solution of the bisulphite and cooling, **normal sodium sulphite**, $Na_2SO_3,7H_2O$, crystallises out,

$$NaOH + NaHSO_3 = Na_2SO_3 + H_2O.$$

On a large scale, the sulphite is prepared by passing sulphur dioxide through crystals of washing soda,

$$Na_2CO_3,10H_2O + SO_2 = Na_2SO_3 + CO_2 + 10H_2O.$$

It is used as an antichlor and as an antiseptic.

Sodium Sulphate, Na_2SO_4.

(*a*) *Manufacture.*—Normal **sodium sulphate**, Na_2SO_4, is manufactured in a crude form as SALT-CAKE in the Leblanc soda process (p. 569) and is used in the manufacture of glass. It is also formed as a by-product in the manufacture of ammonium nitrate from ammonium sulphate and sodium nitrate (p. 606),

$$(NH_4)_2SO_4 + 2NaNO_3 = Na_2SO_4 + 2NH_4NO_3.$$

The **decahydrate**, $Na_2SO_4,10H_2O$, is called GLAUBER'S SALT and is used in medicine as a purgative and diuretic. It can be made by double

decomposition with salt of saline residues containing magnesium sulphate,

$$2NaCl + MgSO_4 + 10H_2O = Na_2SO_4,10H_2O + MgCl_2;$$

the decahydrate crystallises out at a low temperature, whilst the magnesium chloride remains in solution.

(*b*) *Hydrates.*—Sodium sulphate forms two hydrates, the **hepta-hydrate**, $Na_2SO_4,7H_2O$, and the **decahydrate**, $Na_2SO_4,10H_2O$. The decahydrate, $Na_2SO_4,10H_2O$, crystallises from cold water in large, colourless, transparent crystals, and is the stable form of the salt up to 32·383°. Above this temperature, the anhydrous salt, Na_2SO_4, separates and is remarkable in that its solubility diminishes with rise of temperature (Fig. 220*b*). The anhydrous salt is also formed when the decahydrate is heated above 32·383° and thereby decomposed into a mixture of the anhydrous salt and its saturated solution; this decomposition is described as the "melting of the decahydrate in its water of crystallisation"; the temperature at which it takes place is so well defined that it can be used as an additional fixed point for standardising thermometers.

When the crystals of the decahydrate are exposed to dry air, they effloresce and become covered with a white powder consisting of the anhydrous salt. This efflorescence is due to the fact that the vapour pressure of the water of crystallisation of the hydrate at the ordinary temperature generally exceeds the pressure of the water vapour in the air, so that water escapes as vapour and the salt becomes dehydrated; when, however, the air is saturated with moisture, as on a very damp day, the reverse change occurs and the anhydrous salt becomes hydrated. Above 32·383°, the vapour pressure of the water in the decahydrate exceeds that of the saturated solution; the decahydrate cannot exist above this temperature, therefore, but loses water, becomes anhydrous, and melts in its water of crystallisation as described in the preceding paragraph.

When a solution of sodium sulphate is prepared at a temperature slightly above 32°, so that all traces of the solid decahydrate are destroyed, it is possible, by allowing the solution to cool quietly in a flask protected from dust by a plug of cotton-wool, to keep the salt in solution and to prevent entirely the separation of crystals. The cold solution contains far more sodium sulphate than it can ordinarily hold at that temperature when saturated with regard to $Na_2SO_4,10H_2O$, namely, about 50 per cent. of Na_2SO_4 instead of 13·2 per cent.; it is therefore described as a SUPERSATURATED SOLUTION. On shaking the supersaturated solution, or adding a minute crystal of the decahydrate, $Na_2SO_4,10H_2O$, the excess of this salt separates out very quickly and the solution sets to a solid mass of crystals. The condition of equilibrium which exists in a supersaturated solution is peculiar, since it is liable to be upset by a mere trace of crystalline dust, but unless this is

introduced it can persist indefinitely. As this condition is not wholly unstable, it is distinguished as METASTABLE EQUILIBRIUM (compare p. 8).

The **heptahydrate**, $Na_2SO_4,7H_2O$, which is more soluble than either of the above salts, can only exist in a metastable condition, like a supersaturated solution. It separates sometimes from supersaturated solutions below 12°, and can be precipitated from such solutions by the addition of alcohol.

(*c.*) *Acid Sulphates.*—**Sodium hydrogen sulphate**, $NaHSO_4$, or **sodium bisulphate**, is obtained as an intermediate product in the manufacture of salt-cake (p. 569). It also appears as a final product in the manufacture of nitric acid, by the action of sulphuric acid on sodium nitrate,

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3,$$

and is then known as NITRE-CAKE. It crystallises from water as a **monohydrate**, and has a pronounced acid reaction. When alcohol is added to an aqueous solution of the bisulphate, neutral sodium sulphate is precipitated and sulphuric acid is set free,

$$2NaHSO_4 = H_2SO_4 + Na_2SO_4 ;$$

but when extracted with dry alcohol in the absence of water it leaves behind the **sesquisulphate**, $Na_2SO_4,NaHSO_4$; this is probably an important constituent of commercial nitre-cake, which contains much less acid than the bisulphate, $NaHSO_4$. When heated, it is converted into **sodium pyrosulphate**, $Na_2S_2O_7$, and on further heating gives the normal sulphate and sulphur trioxide,

$$2NaHSO_4 = Na_2S_2O_7 + H_2O$$
$$Na_2S_2O_7 = Na_2SO_4 + SO_3.$$

Nitre-cake has been used largely as a substitute for sulphuric acid, *e.g.*, in "pickling" sheet-iron before tinning it, in the manufacture of gas for aerated waters, etc. The conversion of nitre-cake into sodium sulphate by neutralisation with caustic soda waste was an economical operation when nitre-cake was being produced in excessive quantities and sodium sulphate was difficult to procure.

Sodium Salts containing Two Atoms of Sulphur.

(*a*) **Sodium disulphide**, Na_2S_2, is the simplest of the polysulphides described above and corresponds with the peroxide, Na_2O_2.

(*b*) **Sodium thiosulphate,** $Na_2S_2O_3,5H_2O$, is commonly but incorrectly called "hyposulphite* of soda" or "hypo." It can be manufactured from the residues of calcium sulphide obtained in the Leblanc soda process. These are oxidised by air to calcium thiosulphate, which is extracted by boiling water ; on adding sodium sulphate to the solution, calcium sulphate is precipitated and a solution of sodium thiosulphate

* This name was given to the salt because the monohydrate, $Na_2S_2O_3,H_2O$, was mistaken for an acid hyposulphite, $NaHSO_2$.

is obtained, which on filtering and concentrating gives crystals of the **pentahydrate**, $Na_2S_2O_3,5H_2O$,

$$CaS_2O_3 + Na_2SO_4 = CaSO_4 + Na_2S_2O_3.$$

Sodium thiosulphate can also be obtained by dissolving sulphur in an aqueous solution of sodium sulphite,

$$Na_2SO_3 + S = Na_2S_2O_3.$$

The pentahydrate dissolves in less than its own weight of water even at 0°. When heated, it melts in its water of crystallisation, then loses water, and finally decomposes with liberation of sulphur. On adding acid, sulphur dioxide is liberated and sulphur is deposited gradually,

$$Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + S + H_2O.$$

The separation of sulphur distinguishes the thiosulphate from the ordinary sulphite, which also liberates sulphur dioxide under these conditions. Sodium thiosulphate rapidly absorbs chlorine or bromine, and decolorises solutions of iodine quantitatively, according to the equation

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6,$$

sodium tetrathionate, $Na_2S_4O_6$, being formed in each case; this action is used in volumetric analysis. Sodium thiosulphate is used in photography for "fixing" (p. 863), and in the extraction of silver from its ores (p. 845), on account of its property of dissolving silver chloride or bromide,

$$Na_2S_2O_3 + AgCl = NaAgS_2O_3 + NaCl.$$

(*c*) **Sodium hydrosulphite,** $Na_2S_2O_4$.—Unnecessary confusion has been caused by describing this salt (as well as the thiosulphate) as "sodium hyposulphite," a name which should obviously be reserved for a salt such as Na_2SO_2 containing less oxygen than the sulphite, rather than more sulphur. It is formed by the action of sulphur dioxide on sodium hydride (p. 558), and is prepared commercially by dissolving zinc in a solution of sodium hydrogen sulphite,

$$Zn + 4NaHSO_3 = ZnSO_3 + Na_2SO_3 + Na_2S_2O_4 + 2H_2O.$$

The zinc and sodium sulphites which are formed as by-products crystallise out in the form of a double-salt, and the solution contains the hydrosulphite. The zinc salt can be prepared by direct combination of zinc with sulphur dioxide,

$$Zn + 2SO_2 = ZnS_2O_4,$$

and is perhaps an intermediate product in the action shown in the preceding equation. Sodium hydrosulphite is a far more powerful reducing agent than sulphurous acid; it is used largely in dyeing for the reduction of indigo (hydrosulphite vat), and its aqueous solutions are used (with indigo as an indicator) to estimate oxygen dissolved in water.

It is oxidised readily by moist air to sodium metabisulphite,

$$2Na_2S_2O_4 + O_2 = 2Na_2S_2O_5.$$

It also combines with formaldehyde, CH_2O, to form additive compounds derived from $NaHSO_3$ and $NaHSO_2$,

$$2CH_2O + Na_2S_2O_4 + H_2O = HO{\cdot}CH_2{\cdot}SO_2{\cdot}ONa + HO{\cdot}CH_2{\cdot}SO{\cdot}ONa\ ;$$

the latter compound, **sodium formaldehyde-sulphoxylate**, is a derivative of a true hyposulphite, $NaHSO_2$, and is a more powerful reducing agent than the hydrosulphite from which it is prepared.

(*d*) **Sodium metabisulphite**, $Na_2S_2O_5$, has been described above as formed by loss of water from sodium bisulphite.

(*e*) **Sodium dithionate**, $Na_2S_2O_6$, can be prepared by double decomposition from the manganese salt, MnS_2O_6, which is formed (with manganous sulphate, $MnSO_4$) by the action of sulphur dioxide on manganese dioxide suspended in water,

$$MnO_2 + SO_2 = MnSO_4$$
$$MnO_2 + 2SO_2 = MnS_2O_6\ .$$

(*f*) **Sodium pyrosulphate**, $Na_2S_2O_7$, has been described above as formed by loss of water from sodium bisulphate.

(*g*) **Sodium perdisulphate**, $Na_2S_2O_8$ (sometimes called Marshall's sodium persulphate, to distinguish it from Caro's permonosulphate, $NaHSO_5$, p. 348), is formed as an anode product during the electrolysis of sodium hydrogen sulphate. The formation of the acid can be shown in two stages,

$$NaHSO_4 = \overset{+}{Na} + \overset{-}{HSO_4}, \text{ compare } NaCl = \overset{+}{Na} + \overset{-}{Cl},$$
$$2\mathit{HSO}_4 = H_2S_2O_8, \qquad \text{compare } 2\mathit{Cl} = Cl_2.$$

The sodium salt is too soluble to crystallise out readily and is usually converted into the less soluble potassium or ammonium salt.

Other Oxygen Salts.

Sodium Nitrate, $NaNO_3$.

(*a*) *Preparation.*—This salt, commonly known as NITRE or CHILE SALTPETRE, occurs as a widespread deposit in the desert lands of Chile, Peru, and Bolivia, where it is found mixed with soil and covered with layers of clay containing gypsum. The nitre beds have a width of 2 miles and a thickness of 3 to 15 feet and stretch over a distance of 150 miles. The crude CALICHE extracted from them contains up to 65 per cent. of sodium nitrate, together with potassium nitrate (2 to 15 per cent.), sodium chloride (up to 20 per cent), sodium iodate, sodium chlorate and perchlorate, and gypsum. After refining by crystallisation from boiling water, the product contains 95 per cent. of sodium nitrate, with about 1 to 2 per cent. of sodium chloride and smaller quantities of sodium sulphate and perchlorate.

(*b*) *Properties.*—Sodium nitrate melts at 308°. Its crystalline form is rhombohedral and resembles that of calcite (p. 630), but differs from that of potassium nitrate, which only changes from an orthorhombic to a rhombohedral form above 129° : even then the two nitrates have only a very limited power of forming solid solutions with one another. The eutectic mixture of sodium nitrate and potassium nitrate contains approximately molecular proportions of the two salts, melts at 218° (Fig. 221), and is used as a bath for standardising thermometers ; the melting-point can be lowered still further by the addition of a third nitrate, *e.g.*, a mixture of lithium nitrate 30 per cent., sodium nitrate 14 per cent., and potassium nitrate 56 per cent. melts at 120° C. Sodium nitrate is very soluble in water, the solubility increasing rapidly with the temperature, from 42 per cent. of the weight of the saturated solution at 0° to 64 per cent. at 100°.

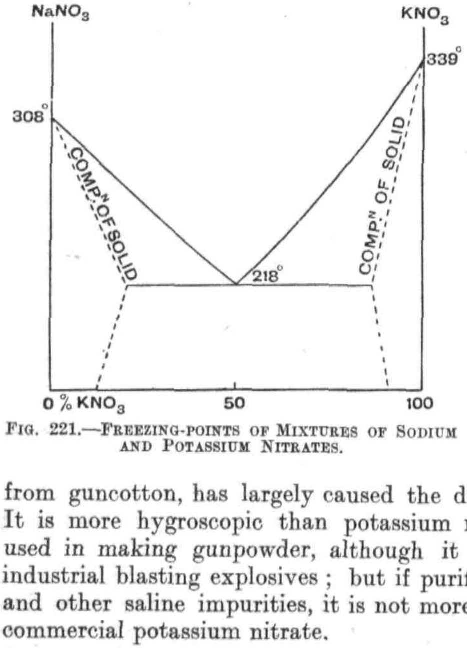


FIG. 221.—FREEZING-POINTS OF MIXTURES OF SODIUM AND POTASSIUM NITRATES.

(*c*) *Uses.* — Enormous quantities of sodium nitrate are exported from Chile, mainly for use as a fertiliser (to supply nitrogen) in agriculture. It is also used for the manufacture of nitric acid, of sodium nitrite, and of potassium nitrate for the preparation of gunpowder, although the use of smokeless powders, prepared from guncotton, has largely caused the decline of this last industry. It is more hygroscopic than potassium nitrate and is therefore not used in making gunpowder, although it is a constituent of some industrial blasting explosives ; but if purified until free from chlorides and other saline impurities, it is not more hygroscopic than unrefined commercial potassium nitrate.

Sodium Nitrite, $NaNO_2$.

This salt is prepared by adding pieces of lead to fused sodium nitrate ; the fused mass is added gradually to water, and the sodium nitrite is extracted from the litharge formed by oxidation of the lead,

$$NaNO_3 + Pb = PbO + NaNO_2.$$

The solution is neutralised with nitric acid to remove traces of sodium hydroxide formed during the action, concentrated to a density of 1·42,

and allowed to crystallise. After a further crystallisation, the salt contains about 98 per cent. of $NaNO_2$.

Another method which has been applied commercially consists in mixing a concentrated solution of sodium nitrate with quicklime and passing sulphur dioxide through the mixture; insoluble calcium sulphate is formed and sodium nitrite remains in solution,

$$NaNO_3 + SO_2 + CaO = NaNO_2 + CaSO_4.$$

Large quantities of sodium nitrite are also prepared in Norway by the absorption in soda of the nitrous gases obtained by oxidation of atmospheric nitrogen (p. 405).

Sodium nitrite is very soluble in water, but crystallises more readily than potassium nitrite. It forms small transparent rhombohedra, and under ordinary atmospheric conditions is not deliquescent.

The salt is used in large quantities as a source of nitrous acid for "diazotisation" (compare p. 397) in the manufacture of dyes.

Sodium Phosphates.

(*a.*) **Trisodium phosphate** or tertiary sodium phosphate, $Na_3PO_4,12H_2O$, gives solutions which are strongly alkaline and absorb carbon dioxide from air.

(*b.*) **Disodium hydrogen phosphate** or secondary sodium phosphate crystallises from cold water as $Na_2HPO_4,12H_2O$, but above 35° with only $2H_2O$. The solution is faintly alkaline to litmus and to phenolphthalein. At 300°, it gives **sodium pyrophosphate**,

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O,$$

which crystallises from water as a **decahydrate**, $Na_4P_2O_7,10H_2O$.

Commercial sodium phosphate, $Na_2HPO_4,12H_2O$, is obtained by digesting rock phosphate or calcium phosphate with dilute sulphuric acid, filtering the solution of phosphoric acid from calcium sulphate, and adding sodium carbonate until there is no further effervescence; the further precipitate of chalk and gypsum which is then formed is removed by filtration and the solution is concentrated and allowed to crystallise.

(*c.*) **Sodium dihydrogen phosphate** or primary sodium phosphate, NaH_2PO_4,H_2O, has an acid reaction to litmus and phenolphthalein, but is neutral to methyl-orange. At 200°, it gives **disodium pyrophosphate**, $Na_2H_2P_2O_7$,

$$2NaH_2PO_4 = Na_2H_2P_2O_7 + H_2O,$$

and at 250° **sodium metaphosphate**, $NaPO_3$,

$$NaH_2PO_4 = NaPO_3 + H_2O.$$

Sodium Borate and Perborate.

Sodium pyroborate, $Na_2B_4O_7,10H_2O$, is found as BORAX in Thibet and in California, and is purified by recrystallisation from water. Borax

is also made from boric acid obtained from the fumaroli of Tuscany (p. 515); this is fused with half its weight of soda-ash and lixiviated with water; on cooling, borax crystallises from the solution. Borax can also be prepared from BORONATROCALCITE, $Na_2B_4O_7,2CaB_4O_7,18H_2O$, by fusing with soda-ash and extracting the product with water,

$$Na_2B_4O_7,2CaB_4O_7 + 2Na_2CO_3 = 3Na_2B_4O_7 + 2CaCO_3.$$

It can be prepared in the same way from COLEMANITE, $Ca_2B_6O_{11},5H_2O$, a calcium borate found in California; or this mineral may be converted into borax more economically by heating it to redness with sodium sulphate,

$$2Ca_2B_6O_{11} + 3Na_2SO_4 = 3CaSO_4 + CaO + 3Na_2B_4O_7.$$

Sodium pyroborate crystallises from water at all temperatures below 60° as the **decahydrate**, $Na_2B_4O_7,10H_2O$, which constitutes ordinary or PRISMATIC BORAX. The **pentahydrate**, $Na_2B_4O_7,5H_2O$, separates as OCTAHEDRAL BORAX at temperatures above 60°.

A solution of borax in water has an alkaline reaction, owing to hydrolysis of the salt (compare sodium carbonate, p. 574), and can be titrated against an acid by using methyl-orange as an indicator. Borax is therefore used instead of soap or soda as a cleansing agent, and in dyeing when a weak alkali is required. Its low melting-point, 741°, has led to its use as a flux, and in brazing and soldering, where the excess of boric acid which it contains enables it to dissolve metallic oxides and thus to clean the surfaces of the metal. Its power to dissolve metallic oxides as borates is also used in analysis, where the coloration of a BORAX BEAD is used as a qualitative test for certain metals (compare microcosmic salt, p. 608).

Sodium perborate, $Na_2B_4O_8,10H_2O$, or perhaps $NaBO_3,4H_2O$, has found considerable application as a bleaching agent, *e.g.*, in laundry work, and as a vigorous antiseptic. It is prepared by dissolving sodium peroxide in ice-cold water, adding boric acid, and passing carbon dioxide (or flue gas) through the mixture. The crystals which separate are washed with alcohol and dried at 50°.

Sodium Silicate.

By fusing together silica and sodium carbonate a **sodium metasilicate**, Na_2SiO_3, is obtained, which forms a series of crystalline hydrates containing from 1 to $9H_2O$; this substance when dissolved in water has a strongly alkaline reaction, owing to hydrolytic dissociation.

SOLUBLE SODA GLASS, OR WATER GLASS, is obtained by fusing together 180 parts of white sand, 100 parts of soda-ash, and 3 parts of charcoal in a reverberatory furnace. The product is usually dissolved in water under pressure in an autoclave, giving a viscous, syrupy liquid; but by grinding it to pass a sieve with 50 meshes to the linear inch, soaking with 25 to 38 per cent. of its weight of water, heating

slowly to 70° and then for four hours at 100°, a product is obtained which can be ground to a permanent powder and yet is readily soluble in cold water. Another method of manufacture consists in heating powdered flint with hot concentrated sodium hydroxide under pressure. The solution probably consists of a mixture of different sodium silicates; when exposed to the air, it absorbs carbon dioxide, and gelatinous silicic acid is precipitated.

Sodium silicate is used in fresco-painting, as a cement in joining broken surfaces of porcelain, as an adhesive for cardboard boxes, etc., and as an adulterant of soap.

Detection, Estimation, and Atomic Weight of Sodium.

Minute traces of sodium can be detected by means of the characteristic yellow doublet in its spectrum.

Insoluble salts of sodium are very uncommon. By adding an aqueous solution of potassium antimonate, $KSbO_3$, the metal can be precipitated as **sodium pyroantimonate**, $Na_2H_2Sb_2O_7,6H_2O$, from aqueous solutions up to a dilution of 1 part in 10,000, but this test can only be used in the absence of lithium and ammonium salts, and of salts of the alkaline earths. By means of BALL'S REAGENT, prepared by adding bismuth nitrate and cæsium nitrate to a solution of pure potassium nitrite (made from the carbonate by the action of nitrous fumes), sodium can be precipitated as the **ternary nitrite,**

$$6NaNO_2,9CsNO_2,5Bi(NO_2)_3,$$

and estimated even in the presence of large quantities of salts of the other alkali metals and of the alkaline earths.

Sodium is often estimated merely "by difference." It can, however, be separated by precipitating all other metals and weighed in the form of the chloride or sulphate.

The atomic weight of sodium is based on exact determinations of the ratios NaCl : AgCl : Ag, *e.g.*, by titration of sodium chloride against a solution of pure silver in nitric acid, without using an indicator, the point of neutralisation being judged by the absence of any cloud on the addition of a further drop of the silver solution to the salt solution.

19. POTASSIUM. K = 39·10.

Occurrence of Potassium.

(*a*) *Silicates.*—Potassium and sodium are equally abundant in igneous rocks which contain 2·5 per cent. each of these two metals, mainly in the form of silicates. The most important of these is **potassium alumino*tri*silicate,** $KAlSi_3O_8$ (compare $NaAlSi_3O_8$), which under the name of POTASH FELSPAR or ORTHOCLASE is a principal constituent of granite. Lavas, on the other hand, and rocks less rich in silica often contain their potassium in the form of **potassium**

aluminodisilicate or LEUCITE, $KAlSi_2O_6$. The corresponding **potassium ferridisilicate**, $KFeSi_2O_6$, is found as GLAUCONITE on the bed of the ocean. Elimination of two-thirds of the potash and silica from felspar by weathering or hydrolysis converts it into MUSCOVITE (a form of MICA),

$$\underset{\text{Felspar}}{3KAlSi_3O_8} + H_2O + CO_2 = \underset{\text{Muscovite}}{KH_2Al_3Si_3O_{12}} + K_2CO_3 + 6SiO_2,$$

whilst a total elimination of the potash with two-thirds of the silica turns it into kaolinite or china clay,

$$\underset{\text{Felspar}}{2KAlSi_3O_8} + 2H_2O + CO_2 = \underset{\text{Kaolinite}}{H_4Al_2Si_2O_9} + K_2CO_3 + 4SiO_2.$$

It is commonly assumed that the sodium salts in the ocean have been washed out from the land and are therefore derived ultimately from the weathering of igneous rocks; the age of the ocean has indeed been calculated from its sodium content and the rate of influx of sodium salts in river water (after allowing for the circulation of salt spray near the coast) to be about 100 million years. It is therefore remarkable that the ratio Na : K, which is 1 : 1 in the rocks, becomes 4 : 1 in the rivers and 30 : 1 in the ocean. This difference appears to be due

(i) To the selective retention of potassium salts by clay, *e.g.*, by reconversion of kaolinite into potash-mica or potash-felspar, or by adsorption on the surface of the minute or "colloidal" particles of clay.

(ii) To the selective precipitation of potassium from oceanic water as glauconite, $KFeSi_2O_6$.

Whatever its cause, this differentiation of sodium and potassium has made common salt the most abundant and cheapest of soluble salts, whilst soluble potassium salts are relatively scarce and costly.

(*b*) *Stassfurt Deposits.*—Sea-water contains less than 0·1 per cent. of potassium salts, but when it is evaporated these are concentrated in the mother liquors, and in very rare instances have been crystallised out, as double salts of **potassium sulphate**, K_2SO_4, and **potassium chloride**, KCl, and preserved in the upper layers of the salt-beds (p. 560). The principal source of soluble potassium salts has been for many years the Stassfurt mines, in the province of Magdeburg, Prussia, producing about 5 million tons of crude potassium salts annually. These supplies are, however, now being supplemented by the equally important deposits in Alsace; soluble potassium salts are also being recovered from the dust of blast furnaces and cement kilns, the yield being increased by adding common salt to the raw materials in order to displace their potassium by sodium.

The principal zones in the Stassfurt salt-beds are as follows:

(i) **Salt Clay**, forming the top layer of the beds,		5 to 10 metres.
(ii) **Carnallite zone,** $KMgCl_3,6H_2O$	55%	15 to 40 metres.
with common salt, NaCl	25%	
kieserite, $MgSO_4,H_2O$	16%	
bischofite, $MgCl_2,6H_2O$, etc.	4%	

(iii) **Kieserite zone,** $MgSO_4,H_2O$	17%	
with common salt, $NaCl$	65%	
carnallite, $KMgCl_3,6H_2O$	13%	
bischofite, $MgCl_2,6H_2O$	3%	
anhydrite, $CaSO_4$	2%	
(iv) **Polyhalite zone,** $2CaSO_4,Mg(SO_4K)_2,2H_2O$	7%	150 to 1000 metres.
with common salt, $NaCl$	91%	
bischofite, $MgCl_2,6H_2O$	1%	
anhydrite, $CaSO_4$	1%	
(v) **Rock salt,** $NaCl$	96 to 91%	
with anhydrite, $CaSO_4$	4 to 9%	

(vi) **Anhydrite,** $CaSO_4$, and **Gypsum,** $CaSO_4,2H_2O$.

These zones must have been laid down horizontally, but are now steeply inclined and folded. The lowest zone of GYPSUM, $CaSO_4,2H_2O$, represents the crystallisation of calcium sulphate as a dihydrate from sea-water not yet saturated with salt. The principal salt zone contains alternate layers of ROCK-SALT, $NaCl$, and ANHYDRITE, $CaSO_4$ (about 10,000 layers of each salt), and represents the crystallisation of calcium sulphate in an anhydrous form from a solution already saturated with salt. In the POLYHALITE zone, the calcium sulphate has carried down potassium magnesium sulphate in the form of a double salt, $2CaSO_4,Mg(SO_4K)_2,2H_2O$. In the KIESERITE zone, magnesium sulphate has crystallised out from a concentrated mother liquor with a single molecule of water as $MgSO_4,H_2O$. Finally, in the CARNALLITE zone the magnesium and potassium salts have crystallised out as the double chloride, $KMgCl_36H_2O$, whilst the excess of magnesium chloride has separated as BISCHOFITE, $MgCl_2,6H_2O$. These very soluble salts have been protected by a layer of salt clay, covered by 30 to 80 metres of anhydrite and by a further layer of younger rock salt (without potassium salts), which is protected in its turn by layers of shale, clay, and drift. The secondary action of water on the original deposits may give KAINITE, $MgSO_4,KCl,3H_2O$, and SCHÖNITE, $Mg(SO_4K)_2,6H_2O$, whilst the complete removal of magnesium chloride may leave a residue of SYLVINE, KCl.

(c) *Organic Compounds.*—Potassium is an indispensable constituent of plants, and cannot be replaced completely by sodium. The fertility of soils therefore depends very largely on the soluble potassium salts which they contain, although soluble phosphates and soluble compounds of nitrogen are equally essential; a soil derived from granite, which still contains particles of felspar, is usually well supplied with soluble potassium salts by the weathering action of water and carbon dioxide. The ashes of land plants consist largely of **potassium carbonate,** K_2CO_3, which was formerly extracted in large quantities from the ashes and sold as POT-ASH. Some plants contain potassium salts of organic acids in notable proportions, *e.g.*, **potassium hydrogen tartrate** or cream of tartar, $KHC_4H_4O_6$, in the grape, and **potassium hydrogen oxalate,** KHC_2O_4, in the sorrel. The "suint," or sweat of sheep,

contains about one-third of its weight of potassium salts, and potash can be obtained from the liquors in which wool has been washed to an extent which pays for the cost of washing. Potassium salts are also obtained from the uncrystallised mother liquors produced in the manufacture of sugar from beet-root, a plant which needs large quantities of potash-manure for its growth and therefore contains a relatively large proportion of potassium.

Metallic Potassium.

(*a*) *Preparation.*—Potassium was formerly prepared by heating potassium carbonate with wood charcoal at a white heat,

$$K_2CO_3 + 2C = 2K + 3CO.$$

This method was dangerous, owing to the formation of an explosive potassium carbonyl, $(KCO)_6$, and potassium is now prepared by electrolysis in the same way as sodium (p. 556).

(*b*) *Physical Properties.*—Potassium is a light, soft, lustrous metal, but tarnishes quickly on exposure to air. It melts at 62·5°, boils at 757°, and its density is 0·86. The eutectic alloy of 23 per cent. of sodium with 77 per cent. of potassium melts at − 12·5°.

(*c*) *Chemical Properties.*—In its chemical properties potassium resembles sodium very closely, but is rather more active. Thus, if a piece of potassium be thrown into water it decomposes it, forming potassium hydroxide and hydrogen, and evolves so much heat that the hydrogen burns and the potassium bursts into flame and produces an explosion.

$$2K + 2H_2O = 2KOH + H_2.$$

(*d*) *Combination with Hydrogen.*—When hydrogen is passed over potassium at 360°, **potassium hydride**, KH, is formed in slender white needles. It is extremely sensitive to the action of moist air, which decomposes it with liberation of hydrogen ; it is also decomposed into its constituents when heated alone to a temperature below a red heat. It combines with carbon dioxide in the cold to form potassium formate, HCO_2K,

$$CO_2 + KH = H{\cdot}CO{\cdot}OK,$$

and with sulphur dioxide to form potassium hydrosulphite,

$$2KH + 2SO_2 = K_2S_2O_4 + H_2.$$

The hydrides formerly described as K_2H and K_4H are probably non-existent.

(*e*) *Action on Ammonia.*—Potassium, like sodium, dissolves in anhydrous liquid ammonia, forming a blue solution. When heated in a current of ammonia, it gives **potassamide**, KNH_2, a compound resembling sodamide (p. 558), which melts at 270° and sublimes in a current of ammonia at 400°.

Compounds of Potassium.

The principal difference between potassium and sodium is found in the smaller solubility of its salts, to which rule potassium carbonate is, however, a notable exception; potassium hydroxide also is more soluble than sodium hydroxide. It is for this reason that, in cases where the acid radical of a salt has a high commercial value, potassium salts are so often prepared in preference to the more soluble and less easily isolated sodium salts. Important examples of this use of potassium are:

Potassium bromide,	KBr
,, iodide,	KI
,, chlorate,	$KClO_3$
,, perchlorate,	$KClO_4$
,, ferrocyanide,	$K_4FeC_6N_6$
,, ferricyanide,	$K_3FeC_6N_6$
,, chromate,	K_2CrO_4
,, dichromate,	$K_2Cr_2O_7$
,, persulphate,	$K_2S_2O_8$
,, permanganate,	$KMnO_4$
,, aluminium sulphate,	$KAl(SO_4)_2,12H_2O$

The smaller solubility of potassium nitrate and its smaller tendency to absorb water are also responsible for its use in preference to sodium nitrate in gunpowder. It is even possible that the essential part played by potassium in plant life may depend on the separation of the potassium salt of some organic acid where the corresponding sodium salt would merely accumulate in solution in the plant-juices. The sparing solubility of the potassium salts, which they share with the ammonium salts, is also made use of in analysis (see below).

COMPOUNDS CONTAINING HALOGENS.

Potassium Chloride, KCl.

(*a*) *Occurrence.*—This salt is found in the Stassfurt beds as SYLVINE, KCl, and in larger quantities in the form of CARNALLITE, $MgCl_2,KCl,6H_2O$ or $KMgCl_3,6H_2O$.

(*b*) *Preparation.*—Carnallite can be broken down into potassium chloride and magnesium chloride by treatment with hot water, when the potassium salt separates on cooling, whilst the more soluble magnesium salt remains in solution. In actual manufacture, the carnallite is treated with the mother liquors from other processes of the manufacture. The crude potassium chloride prepared in this way is purified by washing carefully with water, and contains from 80 to 90 per cent. of KCl. By recrystallisation, a pure product can be obtained.

(*c*) *Properties.*—Potassium chloride resembles sodium chloride very

closely, but has a cooling saline taste quite distinct from that of common salt. Unlike sodium chloride, it is much more soluble in hot water than in cold, *e.g.*, 100 parts of a saturated solution contain 22 parts of KCl at 0°, 36 parts at 100°, and 44 parts under pressure at 180°. It melts at about 775° (NaCl melts at 800°) and volatilises at a bright red heat.

(*d*) *Uses.*—Large quantities of potassium chloride are used in agriculture, in the manufacture of caustic potash, and in the preparation of other potassium salts, such as potassium chlorate, potassium perchlorate, etc.

Potassium Bromide, KBr.

Potassium bromide can be prepared by the action of bromine on a warm solution of potassium hydroxide,

$$6KOH + 3Br_2 = 5KBr + KBrO_3 + 3H_2O.$$

The solution contains bromate as well as bromide; to convert this bromate into bromide, the solution is evaporated to dryness, a little charcoal added, and the mixture heated,

$$2KBrO_3 + 3C = 2KBr + 3CO_2.$$

On a large scale, the bromide is generally manufactured by the action of bromine and water on iron filings, which produces a bromide of iron; the iron is precipitated by the addition of potassium carbonate and the solution, after filtering from the precipitate of ferric hydroxide, gives crystals of potassium bromide on evaporation.

Potassium bromide forms colourless cubic crystals which are very soluble in water. It is used for the preparation of photographic plates and papers and as a sedative in medicine.

Potassium Iodide, KI.

This salt is obtained in a similar manner to the bromide, and resembles it in properties.

A solution of potassium iodide dissolves iodine, forming the **tri-iodide** KI_3, which has been isolated in the form of black needle-shaped crystals. Solutions of potassium iodide dissolve several other iodides which are insoluble in water; thus mercuric iodide dissolves in the presence of potassium iodide, forming **potassium mercuri-iodide,** $2KI,HgI_2$ or K_2HgI_4.

Potassium Hypochlorite, KClO, resembles sodium hypochlorite.

Potassium Chlorate, $KClO_3$.

(*a*) *Preparation.*—This salt was first prepared by passing chlorine into a hot solution of potassium hydroxide,

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

This method was expensive, involving the use of potassium hydroxide,

five-sixths of which was converted to chloride. On a manufacturing scale, therefore, chlorine was bubbled through milk of lime heated to 40° in cast-iron cylinders fitted with agitators, giving a solution of calcium chloride and calcium chlorate,

$$6Ca(OH)_2 + 6Cl_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O.$$

After filtration, the concentrated solution was decomposed by the addition of potassium chloride, which caused the separation of the less soluble potassium chlorate on cooling,

$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3.$$

The greater part of the chlorine is here employed in producing the valueless calcium chloride, but there is no serious waste of potassium, and the potassium chloride used to precipitate the chlorate is much less costly than the potassium hydroxide used in the original process.

By making use of electrolytic oxidation, the cost of manufacturing potassium chlorate has been more than halved. For this purpose an aqueous solution of potassium chloride is electrolysed at a temperature of 60–70°, under conditions which do not keep the anode and cathode products separate, but allow them to mix freely (contrast potassium hydroxide). Under these conditions, potassium chloride is oxidised at the anode to potassium chlorate, whilst hydrogen gas is evolved at the cathode, the general result of the electrolysis being expressed by the equation

$$KCl + 3H_2O = KClO_3 + 3H_2.$$

Chlorates are also obtained as by-products in the electrolytic manufacture of caustic alkalies when using anodes of magnetic iron oxide which are not attacked by oxygen (p. 566).

(*b*) *Properties.*—Potassium chlorate is only sparingly soluble in cold water, but is much more so in hot water; thus a saturated solution contains 3·2 per cent. of $KClO_3$ at 0°, and 38 per cent. of $KClO_3$ at 104·2°. It melts at 370°, and at a slightly higher temperature decomposes with effervescence, liberating oxygen and forming potassium chloride and perchlorate, probably as the result of two superposed chemical changes,

$$\begin{aligned} 4KClO_3 &= 3KClO_4 + KCl \\ KClO_4 &= KCl + 2O_2 \quad \text{or} \quad 2KClO_3 = 2KCl + 3O_2. \end{aligned}$$

When a small quantity of manganese dioxide is added, the decomposition of the chlorate is complete at a temperature below that of fusion and no perchlorate is formed,

$$2KClO_3 = 2KCl + 3O_2.$$

Certain other oxides, such as CuO and Fe_2O_3, have a similar action, but the oxides of calcium, barium, and lead do not behave in this way.

A solution of potassium chlorate is a powerful oxidising agent, which will oxidise iron and must therefore be evaporated in lead-lined

vessels. It is also reduced quantitatively to the chloride by the action of sulphur dioxide at 100°,

$$KClO_3 + 3SO_2 + 3H_2O = KCl + 3H_2SO_4.$$

When heated with hydrochloric acid, potassium chlorate liberates chlorine and chlorine dioxide and is itself reduced to potassium chloride, *e.g.*, as shown in the equation

$$8KClO_3 + 24HCl = 8KCl + 9Cl_2 + 6ClO_2 + 12H_2O.$$

When acted upon by strong sulphuric acid, the unstable and explosive gas, chlorine dioxide, ClO_2, is again produced,

$$6KClO_3 + 3H_2SO_4 = 3K_2SO_4 + 2HClO_4 + 4ClO_2 + 2H_2O.$$

On account of its powerful oxidising action, potassium chlorate forms a series of dangerous mixtures with combustible substances such as phosphorus, charcoal, and sugar. When mixed with carbon and sulphur, it forms a gunpowder resembling that obtained by using nitre, but unsuitable for general use on account of its excessive sensitiveness ; the first attempt to use it, almost immediately after its discovery by Berthollet in 1788, led to a fatal explosion ; chlorate explosives have therefore been regarded with suspicion ever since, although they have been employed successfully as commercial blasting explosives by merely coating the grains with paraffin wax. Like ammonium nitrate, potassium chlorate is capable of exploding without the addition of oxidisable materials, although only one explosion of this character on a large scale has been recorded.

Potassium chlorate is used in the manufacture of fireworks, of photographic flash-powders (mixed with magnesium and a little red phosphorus), and of matches (p. 423).

Potassium Perchlorate, $KClO_4$.

This salt is formed on carefully heating potassium chlorate,

$$4KClO_3 = 3KClO_4 + KCl;$$

the action is exothermic, and liberates about 63,000 calories.

Potassium perchlorate is prepared commercially by electrolysing a solution of sodium chloride so as to form sodium chlorate, which is converted by further electrolytic oxidation into sodium perchlorate ; to this solution potassium chloride is added so as to precipitate the less soluble potassium perchlorate,

$$NaClO_4 + KCl = KClO_4 + NaCl.$$

Potassium perchlorate is one of the least soluble salts of potassium, since a saturated solution in water contains only 0·7 per cent. of $KClO_4$ at 0°. It is practically insoluble in 95 per cent. alcohol containing 0·2 per cent. of perchloric acid, a fact which is made use of in the estimation of potassium. It melts at about 600°, but loses oxygen at a much lower temperature when manganese dioxide is present.

Potassium perchlorate is used as a source of oxygen in explosives and fireworks. Although containing a higher proportion of oxygen than potassium chlorate, it is a less violent oxidising agent and yields much more insensitive explosives when mixed with paraffin wax, wood-meal, aluminium, zinc, or similar reducing agents. With sulphuric acid, it yields a stable perchloric acid, $HClO_4,2H_2O$, which can be distilled off; potassium chlorate under the same conditions gives the explosive chlorine peroxide, ClO_2.

Oxides, Hydroxide, and Carbonates.

Potassium Oxides.

Dipotassium monoxide, K_2O, is said to be formed on burning potassium with potassium nitrate in the proportions shown in the equation:

$$2KNO_3 + 10K = 6K_2O + N_2.$$

It is described as a grey mass, which dissolves in water, forming potassium hydroxide,

$$K_2O + H_2O = 2KOH.$$

When burnt in oxygen potassium gives the monoxide, K_2O, together with the peroxides, K_2O_2 and K_2O_4. The **dioxide**, K_2O_2, is said to be pink, whilst the **tetroxide**, K_2O_4, is a yellow powder which decomposes at a red heat, giving K_2O and oxygen; its solution behaves like hydrogen peroxide and is a strong oxidising agent.

Potassium Hydroxide, KOH.

Potassium hydroxide can be prepared from potassium carbonate by the action of lime,

$$K_2CO_3 + Ca(OH)_2 = 2KOH + CaCO_3.$$

As in the case of sodium carbonate (p. 564), the action is reversible, and the yield of hydroxide is diminished if the solution of the carbonate is too concentrated. It has been stated, however, that if strontium hydroxide be used in place of lime far more concentrated solutions can be used, whilst the strontium carbonate can be reconverted easily into the hydroxide.

Most of the potassium hydroxide now made is obtained by the electrolysis of solutions of potassium chloride by methods similar to those described under sodium hydroxide.

Potassium hydroxide is freely soluble in water and forms hydrates with 4, 2, and 1 H_2O (Fig. 222). The **tetrahydrate**, $KOH,4H_2O$, separates from solution at temperatures below $-33°$. A solution concentrated so as to contain 58 per cent. of KOH, if cooled to 0°, deposits small rhombohedra of the **dihydrate**, $KOH,2H_2O$, which is the stable form from $-33°$ to $+33°$; it melts in its water of crystallisation and passes into the monohydrate at 33°, when the saturated solution contains 57 per

cent. of KOH. Above 33°, the **monohydrate**, KOH,H_2O, separates from solution.

The anhydrous compound crystallises from solutions concentrated to 90 per cent. KOH, and can also be obtained by dehydrating the solution in a vacuum at 260°. If concentrated by boiling down under atmospheric pressure, the solution yields the anhydrous compound in a molten condition; solutions of this kind, which do not deposit crystals but give a molten product when concentrated by boiling, are sometimes described as INEVAPORABLE SOLUTIONS.

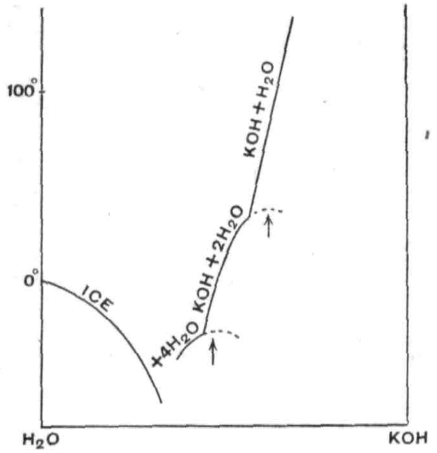


FIG. 222.—EQUILIBRIUM BETWEEN WATER AND THE HYDRATES OF POTASSIUM HYDROXIDE.

The chemical properties of potassium hydroxide are similar to those of sodium hydroxide. It is used in the manufacture of soft soap, and in analysis is preferred to sodium hydroxide as an absorbent of carbon dioxide on account of the greater solubility both of the hydroxide and of the carbonate.

Potassium Carbonate, K_2CO_3.

(*a*) *Preparation.*—(i) This substance forms the principal constituent of the ash of wood and of plants. It was originally obtained from these materials by extracting the ash with water in earthenware pots; hence the name POT-ASH (p. 47). The crude material, obtained by lixiviating the ashes, evaporating the lye to dryness, and calcining the residue, can be purified by redissolving in water, evaporating, and again calcining. The product is then known as PEARL-ASH.

(ii) A similar method of preparation is applied to the final mother liquors obtained from the manufacture of sugar from the sugar beet. These mother liquors are fermented with yeast, so as to destroy the sugar and to yield alcohol, which is distilled off. The liquor remaining is evaporated nearly to dryness in a vacuum. It is then calcined, or heated in retorts so as to recover the by-products such as ammonia and trimethylamine. The solid carbonaceous residue, which contains 30 to 60 per cent. of K_2CO_3, is extracted with water, and the liquor on evaporation yields crude potassium carbonate.

(iii) Considerable quantities of crude potassium carbonate are obtained in France by igniting wine-lees which are too poor to be suitable for the manufacture of tartaric acid, extracting the residue with water,

and purifying as above. The product is a pearl-ash which was formerly known as CALCINED TARTAR.

(iv) In Australia, crude potassium carbonate is obtained by evaporating the water used in wool-washing and calcining the residue; the wool-fat contains a considerable quantity of potassium salts of fatty acids, which, on calcination, are converted into the carbonate.

(v) Potassium carbonate can be prepared from potassium chloride by a process analogous to the Leblanc process for soda; but it cannot be manufactured by an ammonia process, analogous to the Solvay process, owing to the fact that the solubility of potassium hydrogen carbonate is considerably greater than that of the corresponding sodium salt.

(vi) Potassium carbonate is manufactured at Stassfurt by the MAGNESIA PROCESS. This depends on the fact that when carbon dioxide is passed into a solution of potassium chloride in presence of hydrated magnesium carbonate at a temperature of 20°, an insoluble **potassium hydrogen magnesium carbonate**, $MgCO_3,KHCO_3,4H_2O$ or $Mg(CO_3H)CO_3K,4H_2O$, is precipitated,

$$2KCl + 3(MgCO_3,3H_2O)^* + CO_2 = MgCl_2 + 2(MgCO_3,KHCO_3,4H_2O).$$

The sparingly soluble double salt is separated and decomposed by warming with water, or preferably by the action of magnesium oxide at a temperature below 20°,

$$2(MgCO_3,KHCO_3,4H_2O) + MgO = 3(MgCO_3,3H_2O) + K_2CO_3;$$

a solution of potassium carbonate is thus obtained, whilst hydrated magnesium carbonate is precipitated, ready for use with a fresh quantity of potassium chloride. By filtering and evaporating the solution, a potassium carbonate is obtained which is free from sodium salts, since sodium chloride is not precipitated by the magnesium carbonate in this process.

Pure anhydrous potassium carbonate is obtained by igniting potassium hydrogen tartrate (cream of tartar), or pure potassium bicarbonate,

$$2KHCO_3 = K_2CO_3 + CO_2 + H_2O.$$

(*b*) *Properties.*—Potassium carbonate is a white, granular powder which is very soluble in water and deliquesces on exposure to moist air. It separates from solution as a **dihydrate**, $K_2CO_3,2H_2O$, but a **sesquihydrate**, $2K_2CO_3,3H_2O$, can be crystallised out from solution in presence of potassium hydroxide (compare the separation of anhydrite from sea-water saturated with salt). The chemical properties of potassium carbonate are almost identical with those of sodium carbonate.

(*c*) *Uses.*—Potassium carbonate is used in the manufacture of glass (p. 496), and in dyeing.

* Or $HO{\cdot}Mg{\cdot}CO_3H,2H_2O$; see p. 618.

Potassium Hydrogen Carbonate or **Potassium Bicarbonate,** $KHCO_3$.

This salt was first prepared by Black in 1755 by exposing solutions of potassium carbonate to the carbon dioxide of the atmosphere. It is similar to sodium bicarbonate, but is about three times as soluble in water; thus water at 20° dissolves one-third of its weight of $KHCO_3$, but only about one-tenth of its weight of $NaHCO_3$.

OTHER OXYGEN SALTS.

Potassium Sulphate, K_2SO_4.

This salt is manufactured from potassium chloride or sylvine by the action of sulphuric acid, and from kainite, $Mg(SO_4K)_2,MgCl_2,6H_2O$, and schönite, $Mg(SO_4K)_2,6H_2O$, by a process of crystallisation.

It separates from water in anhydrous crystals and thus differs in a marked way from sodium sulphate. It is also much less soluble, requiring ten times its weight of water at 15° to dissolve it.

Enormous quantities are used as a fertiliser, either in the form of the sulphate itself, or as the mineral kainite, or the double salt, $K_2SO_4,MgSO_4,H_2O$, prepared from it, which contains approximately 50 per cent. of K_2SO_4. It is also used in the manufacture of potash alum and potassium carbonate.

Potassium hydrogen sulphate, $KHSO_4$, **potassium sulphite**, K_2SO_3, and **potassium thiosulphate**, $K_2S_2O_3$ (as well as the **sulphide**, K_2S, and **hydrosulphide**, KHS), resemble the corresponding sodium compounds, but are used less extensively.

Potassium Nitrate, KNO_3.

(*a*) *Occurrence.*—This salt, commonly known as NITRE OT SALTPETRE, (p. 46) is found in the soil in various hot countries, but especially in India, where it is obtained by the lixiviation of certain rocks which contain 2·5 to 8 per cent. of KNO_3 (whence the name sal-petræ), and of soils enriched with nitrogenous excrements. It is formed by the decay of nitrogenous organic matter, in contact with alkali, under the influence of a nitrifying organism which oxidises ammoniacal nitrogen to nitric acid. This process is known as NITRIFICATION and was formerly brought about artificially in "nitre plantations"; brushwood was interlaid with manure, strewn with wood ashes and lime, and left exposed to the air for long periods, being watered from time to time with urine or stable drainage. The fermentation of the organic matter produces ammonia, which is oxidised by the nitrifying organisms, utilising atmospheric oxygen, first to nitrite then to nitrate; on extracting with water, a solution of calcium nitrate is obtained, from which the addition of wood ashes (potassium carbonate) precipitates calcium carbonate, leaving a solution of potassium nitrate,

$$Ca(NO_3)_2 + K_2CO_3 = CaCO_3 + 2KNO_3.$$

This solution on evaporation yields crude nitre, which can be purified by recrystallisation.

(*b*) *Manufacture from Sodium Nitrate.*—Saltpetre is also manufactured from sodium nitrate and potassium chloride by the so-called "conversion-process,"

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

A saturated solution of sodium nitrate is mixed with a molecular proportion of potassium chloride and concentrated to density 1·50, when practically all the sodium separates as chloride, since sodium chloride is far less soluble in the hot solution than any of the other salts. On cooling, the clear solution deposits nearly pure potassium nitrate, because potassium nitrate is less soluble in the cold than any of the other salts. The solubilities of the different salts which determine this result are shown in Fig. 223. Before the war, some 20,000 tons of saltpetre were exported from India, mainly from Bengal, whilst nearly 50,000 tons were manufactured by conversion.

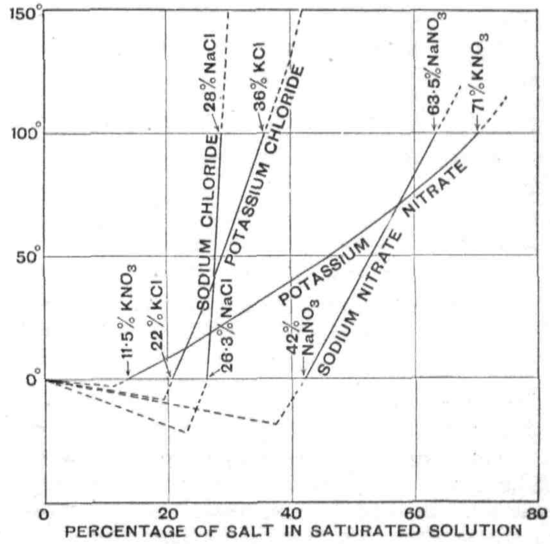


FIG. 223.—SOLUBILITIES OF SODIUM AND POTASSIUM CHLORIDE AND NITRATE.

(*c*) *Properties.*—Potassium nitrate is dimorphous. It usually crystallises, without water of crystallisation, in orthorhombic prisms, which are isomorphous with one form of ammonium nitrate; but on evaporating a few drops of a hot solution, rhombohedral crystals separate, which are isomorphous with those of sodium nitrate. These are, however, unstable and when touched are converted into a mass of small orthorhombic crystals. The orthorhombic form is stable up to 129·5°, and the rhombohedral form above this temperature.

The properties of potassium nitrate are similar to those of sodium nitrate, but it is less soluble and therefore less hygroscopic. This enables it to be used directly in the manufacture of GUNPOWDER, which consists of a mixture of about 75 per cent. of potassium nitrate, 10 per

cent. of sulphur, and 15 per cent. of wood charcoal, intimately incorporated by grinding them together under heavy rollers in an edge-runner mill during a period of about eight hours. Potassium nitrate is rich in oxygen, and gunpowder depends for its effect on the sudden oxidation of the carbon and sulphur by the oxygen of the nitre, giving rise to a large volume of gaseous products. The experiments of Noble and Abel showed that more than half the products of the explosion of gunpowder are solid compounds, principally potassium carbonate, thiosulphate, and sulphide, which form a dense white smoke, whilst the principal gases are carbon dioxide and nitrogen. Gunpowder as a propellant has now been superseded by SMOKELESS POWDERS, made from guncotton or from mixtures of guncotton with nitroglycerine (for example, cordite), which give only gaseous products, and therefore little or no smoke.

Potassium Nitrite, KNO_2, is obtained by similar methods to those used in making sodium nitrite and forms white, deliquescent crystals.

Detection and Estimation of Potassium.

Potassium, like sodium, can be detected by means of its flame spectrum.

The following salts, which are sparingly soluble in water, can be used for the detection of potassium :

Potassium platinichloride,	K_2PtCl_6
Potassium perchlorate,	$KClO_4$
Potassium cobaltinitrite,*	$K_3Co(NO_2)_6$
Potassium hydrogen tartrate,	$KH(C_4H_4O_6)$.

The reagents used are platinic chloride, $PtCl_4$, perchloric acid, $HClO_4$, sodium cobaltinitrite, $Na_3Co(NO_2)_6$ (p. 799), and tartaric acid, $C_4H_6O_6$.

For quantitative work, potassium is precipitated from aqueous solutions as the platinichloride, or as the perchlorate in presence of alcohol. In organic compounds, potassium can be estimated as the sulphate after ignition with sulphuric acid.

The atomic weight of potassium is based upon exact determinations of the ratios

$$KClO_3 : KCl, \qquad KCl : Ag, \qquad Ag : AgCl.$$

These three ratios give the equivalents of potassium, chlorine, and silver relatively to oxygen (p. 292).

AMMONIUM. NH_4 OR Am = 18·02.

Isomorphism of Sodium, Potassium, and Ammonium Salts.

When ammonia unites with acids, it forms salts which resemble those of the alkali-metals so closely that it is convenient to describe

* The precipitate usually has the composition $K_2NaCo(NO_2)_6.\frac{1}{2}H_2O$.

them with those of the metals of this group. This analogy was recognised in the introduction of the name AMMONIUM by Davy in 1808, and of the symbol Am to represent the compound radical, NH_4, by Berzelius in 1823. The close similarity of these compounds is shown by the isomorphism of the AMMONIUM-SALTS with those of this group of univalent metals. The isomorphism of ammonium phosphate and arsenate with the corresponding salts of sodium and potassium was noted by Mitscherlich in 1820, when he put forward his first observations on isomorphism.

Ammonium salts.	*Sodium salts.*	*Potassium salts.*
$(NH_4)H_2PO_4$	NaH_2PO_4,H_2O	KH_2PO_4
$(NH_4)H_2AsO_4$	NaH_2AsO_4,H_2O	KH_2AsO_4

A similar isomorphism is observed in the alums, thus,

Potash alum.	*Ammonia alum.*
$KAl(SO_4)_2,12H_2O$	$(NH_4)Al(SO_4)_2,12H_2O$.

This isomorphism is remarkable in that five non-metallic atoms are inserted in place of a single atom of a metal without disturbing the crystalline structure. It can, however, be explained readily by the "octet" theory of Lewis and Langmuir (p. 550), since a nitrogen atom (atomic number 7) with 2 inner and 5 outer planetary electrons would have a complete octet of $5 + 4 - 1 = 8$ outer electrons when converted into an ammonium ion NH_4^+ by the *addition* of 4 hydrogen atoms with 1 planetary electron each, and the *loss* of 1 electron on ionisation ; it would then resemble sodium (atomic number 11), which has 2 inner and 9 outer planetary electrons, but loses one on ionisation and has then a complete octet in the outer shell.

Similarity of Ammonium and Potassium Salts.

The ammonium salts approximate more closely to the salts of potassium than to those of sodium or of the other elements of the group. This resemblance is seen in the precipitation in qualitative analysis of the two platinichlorides, $(NH_4)_2PtCl_6$ and K_2PtCl_6, whilst the corresponding sodium salt remains in solution. It is also seen in the commercial preparation of alums containing potassium and ammonium sulphates, where the corresponding sodium alum is rarely prepared, probably on account of its greater solubility and consequent greater difficulty in purification. In the same way, when perchlorates and persulphates are prepared by electrolysis of sodium chlorate and sodium sulphate, they are commonly separated by precipitating them in the form of the potassium or ammonium salt, as formulated below, because the sodium salts are so much more soluble.

Ammonium salts.	*Potassium salts.*
$(NH_4)ClO_4$	$KClO_4$
$(NH_4)_2S_2O_8$	$K_2S_2O_8$

Dissociation and Decomposition of Ammonium Salts.

So long as the ammonium radical, NH_4, remains intact, the chemical properties of the ammonium salts are substantially identical with those of the corresponding salts of sodium or potassium ; but the ammonium salts also undergo many novel and important changes, depending on the fact that the ammonium radical is not an element but a group of atoms, which can be broken down in ways that are quite impossible when the compound radical, NH_4, is replaced by one of the simple metallic radicals, Na, K, etc. These changes may be grouped under the two headings of DISSOCIATION and DECOMPOSITION, according as they are reversible or not. The former class includes the dissociation by heat of salts such as :

Ammonium chloride, $(NH_4)Cl \rightleftharpoons NH_3 + HCl$
Ammonium iodide, $(NH_4)I \rightleftharpoons NH_3 + HI$
Ammonium sulphide, $(NH_4)_2S \rightleftharpoons 2NH_3 + H_2S$

where the corresponding salts of sodium and potassium are stable. The latter class includes the non-reversible decomposition by heat of oxy-salts, such as :

Ammonium nitrate, $(NH_4)NO_3 = N_2O + 2H_2O$
Ammonium nitrite, $(NH_4)NO_2 = N_2 + 2H_2O$
Ammonium dichromate, $(NH_4)_2Cr_2O_7 = N_2 + 4H_2O + Cr_2O_3$,

where the corresponding salts of sodium and potassium are either stable or decompose in a different manner, *e.g.*,

$$2KNO_3 = 2KNO_2 + O_2$$
$$2NaNO_3 = 2NaNO_2 + O_2.$$

Dissociation of ammonium salts may also occur in solution, since although the solutions are neutral they tend to lose ammonia and to develop an acid reaction when boiled.

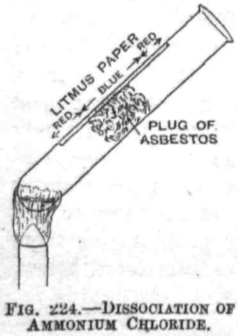


FIG. 224.—DISSOCIATION OF AMMONIUM CHLORIDE.

The dissociation of ammonium chloride may be demonstrated very easily by means of the apparatus shown in Fig. 224. A fragment of the salt is heated in a test-tube provided with a piece of damp red litmus-paper held in place by a plug of asbestos. The ammonia produced by the dissociation of the salt diffuses up the tube more rapidly than the hydrogen chloride ; the litmus inside the plug therefore turns blue. On further heating, the litmus inside the plug becomes red again, whilst a blue colour appears opposite the plug and extends gradually almost to the top of the tube.

The use of ammonium chloride in cleaning metals before soldering, and the solubility of manganese dioxide in ammonium salts as noted by Scheele in 1771, both depend on the

fact that the ammonium radical is not merely compound but contains an oxidisable element, hydrogen,

$$6NH_4Cl + 3MnO_2 = N_2 + 6H_2O + 3MnCl_2 + 4NH_3.$$

Ammonium nitrate and ammonium perchlorate, both of which can be detonated with very great violence, possess this quality in virtue of the fact that they contain loosely-combined hydrogen in the positive radical and loosely-combined oxygen in the negative radical of the same salt. In this respect they resemble nitroglycerine, $C_3H_5(NO_3)_2$, nitrocellulose, and the aromatic nitro-compounds, such as picric acid, $C_6H_2(OH)(NO_2)_3$, and trinitrotoluene, $C_6H_2(CH_3)(NO_2)_3$, which contain in the same molecule both carbon and hydrogen and the oxygen required to burn them.

Ammonium Amalgam.

The close analogy of the ammonium salts to those of sodium and potassium suggests the question whether the ammonium radical can mimic the properties of the alkali metals, not only in combination, but also in the free state. Many attempts have been made to isolate the ammonium radical, but no fundamental advance has been made since Davy in 1808 succeeded in preparing an AMMONIUM AMALGAM by electrolysing ammonium chloride with a mercury cathode (compare the formation of sodium amalgam by the electrolysis of salt in the Castner-Kellner process, p. 565). The same product was obtained by the action of a dilute sodium amalgam on a concentrated solution of sal-ammoniac. The effect upon the mercury was remarkable, since a mere trace of "ammonium" caused the separation from the mercury of arborescent crystals, which rendered the whole mass of a buttery consistency. The solid was not isolated, but Davy proved that when decomposed by heat it liberated two volumes of ammonia to one volume of hydrogen, that is, it gave the decomposition products which would be expected from the ammonium radical,

$$2NH_4 = 2NH_3 + H_2.$$

The exact nature of ammonium amalgam has been a matter of much dispute, but its close analogy to sodium amalgam is too obvious to be overlooked. It may be suggested that, just as the separation of solid crystals from sodium amalgam is generally due to the crystallisation of the compound $NaHg_2$, so perhaps the crystals in ammonium amalgam may be those of an analogous compound of the ammonium radical with mercury, *e.g.*, NH_4Hg_2.

Compounds which may be regarded as analogous to the ammonium radical are formed when the metals of the alkalies or of the alkaline earths are dissolved in liquid ammonia, giving rise to blue products which have been formulated as NH_3Na and NH_3K (p. 381).

COMPOUNDS CONTAINING HALOGENS.

Ammonium Chloride, NH_4Cl.

(*a*) *Preparation.*—This salt, commonly known as SAL-AMMONIAC (p. 46), was prepared in early times as a sublimate by the distillation of camels' dung. Priestley in 1774 prepared it by mixing "alkaline air" with "acid air"

$$NH_3 + HCl = NH_4Cl;$$

the formation of a white cloud on mixing ammonia and hydrogen chloride is still used as a qualitative test for these two gases. It can be prepared by neutralising ammonia liquor from the gas-works with hydrochloric acid or by distilling a mixture of common salt with ammonium sulphate,

$$(NH_4)_2SO_4 + 2NaCl = 2NH_4Cl + Na_2SO_4;$$

a similar double decomposition can be brought about in aqueous solutions by concentrating until sodium sulphate separates. It is formed as a by-product in the manufacture of soda in the ammonia-soda process,

$$NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl,$$

and may become an important product as the result of combining the Haber process for making synthetic ammonia (p. 378) with the Solvay process for making sodium bicarbonate (p. 571).

(*b*) *Physical Properties.*—In its general properties ammonium chloride resembles sodium chloride. It has a sharp, saline taste, which is, however, quite distinct from that of common salt. It dissolves readily in water with a marked lowering of temperature.

(*c*) *Dissociation.*—When heated, ammonium chloride sublimes without melting. The vapour is a mixture of ammonia and hydrogen chloride,

$$NH_4Cl = NH_3 + HCl,$$

which has only one-half the vapour density calculated for the formula NH_4Cl. The two components can be separated by diffusion through a porous diaphragm, but they recombine immediately on cooling; the dissociation of the salt was therefore not suspected until 1857, although the abnormal density of the vapour, and the fact that no contraction occurs when ammonia and hydrogen chloride are mixed at a temperature above the vaporising point of the salt, had been recorded nearly twenty years previously. An apparatus for demonstrating the separation of the two constituents from the vapour is shown in Fig. 224, p. 600.

Baker has proved that dry ammonium chloride can be vaporised without decomposition, and that ammonia and hydrogen chloride, if completely dried, do not unite even at atmospheric temperatures.

(*d*) *Chemical Properties.*—So long as the ammonium radical is not attacked, the chemical properties of sal-ammoniac are similar to those

of common salt. Thus, when acted upon by acids, it liberates hydrogen chloride,

$$2NH_4Cl + H_2SO_4 = (NH_4)_2SO_4 + 2HCl;$$

but, unlike sodium chloride, it is also decomposed by bases, *e.g.*,

$$2NH_4Cl + 2CaO = 2NH_3 + CaCl_2 + Ca(OH)_2.$$

The action shown in this equation can be used for preparing dry ammonia, whilst a similar decomposition by slaked lime in the presence of water is used in recovering the ammonia in the ammonia-soda process.

Ammonium fluoride, NH_4F, has many of the chemical properties of hydrogen fluoride, and like the free acid attacks glass and other silicates. It resembles potassium fluoride in forming an acid salt of the formula NH_4F,HF. **Ammonium bromide**, NH_4Br, and **ammonium iodide**, NH_4I, resemble the corresponding salts of the alkali-metals.

Ammonium perchlorate, NH_4ClO_4, prepared by precipitation from sodium perchlorate, can be exploded by a powerful blow; but as it contains more oxygen than is required to oxidise the hydrogen of the ammonium radical, its power as an explosive can be increased very greatly by mixing it with oxidisable substances.

OXIDES, SULPHIDES AND CARBONATES.

Ammonium Oxide, $(NH_4)_2O$, and Ammonium Hydroxide, $(NH_4)OH$.

The existence of ammonium hydroxide has long been assumed in order to account for the alkaline properties which are developed when ammonia is dissolved in water. Two compounds having the composition $2NH_3,H_2O$ and NH_3,H_2O, melting at $-78°$ and $-77°$ respectively, have recently been isolated by cooling mixtures of ammonia and water to low temperatures (Fig. 150, p. 580); these may be regarded as the **oxide** and **hydroxide** of the radical. An **ammonium peroxide** of the formula $(NH_4)_2O_2,H_2O_2$, has also been isolated by cooling ethereal solutions of ammonia and hydrogen peroxide.

Ammonium Sulphides and Ammonium Hydrosulphide.

These compounds correspond closely with the sodium salts (p. 576).

(*a*) **Ammonium sulphide**, $(NH_4)_2S$, can be prepared by the union of hydrogen sulphide with an excess of gaseous ammonia at $-18°$,

$$2NH_3 + H_2S = (NH_4)_2S.$$

It can also be prepared (compare the sodium salt) by saturating one-half of a quantity of ammonia-liquor with sulphuretted hydrogen and then adding the other half,

$$(NH_4)SH + NH_3 = (NH_4)_2S.$$

It forms colourless crystals, but its solutions soon become yellow by oxidation to polysulphides; finally, ammonium thiosulphate and sulphate are formed.

(*b*) **Ammonium hydrosulphide**, $(NH_4)SH$, is formed when ammonia and sulphuretted hydrogen are mixed together in any proportions,

$$NH_3 + H_2S = (NH_4)SH,$$

but it is completely dissociated again on heating. It can be prepared by saturating aqueous ammonia with sulphuretted hydrogen and crystallised out by cooling to 0°. It forms colourless crystals and dissolves in water to a colourless solution, which is oxidised rapidly in air, with formation of a yellow polysulphide, *e.g.*,

$$4(NH_4)SH + O_2 = 2(NH_4)_2S_2 + 2H_2O.$$

(*c*) The **polysulphides** range in composition from $(NH_4)_2S_2$ to $(NH_4)_2S_7$. **Ammonium disulphide,** $(NH_4)_2S_2$, can be prepared in anhydrous yellow crystals by passing sulphur vapour and sal-ammoniac through a red hot tube.

Ammonium Carbonates.

A "volatile alkali" known as SAL-VOLATILE (p. 48) was prepared in early times by distilling sal-ammoniac with potash or soda. The principal action is probably

$$2NH_4Cl + Na_2CO_3 = (NH_4)_2CO_3 + 2NaCl,$$

but the normal ammonium carbonate shown in this equation is not readily obtained in a pure state. Priestley in 1771 noticed the formation of sal-volatile on mixing "alkaline air" or ammonia with "fixed air" or carbon dioxide,

$$2NH_3 + CO_2 = (NH_3)_2CO_2;$$

this product is not a carbonate, $CO(ONH_4)_2$, which requires the addition of water for its formation,

$$2NH_3 + CO_2 + H_2O = (NH_4)_2CO_3,$$

but an **ammonium carbamate** $NH_2{\cdot}CO{\cdot}ONH_4$ (p. 459), formed from the carbonate by the loss of the molecule of water. Ammonium carbamate, like sal-ammoniac, dissociates when it is sublimed, and no contraction is observed when its gaseous components are mixed at a temperature above the vaporising point of the salt; the vapour-density of the salt is therefore only one-third of that required by the formula given above.

Commercial ammonium carbonate consists mainly of a true **sesquicarbonate,** $(NH_4)_2CO_3,2(NH_4)HCC_3,H_2O$ (contrast sodium sesquicarbonate, $Na_2CO_3,NaHCO_3,2H_2O$, p. 576, which contains only 4/3, instead of 3/2, of an equivalent of acid for each equivalent of alkali); this can be converted by the action of aqueous ammonia into the **normal carbonate**, $(NH_4)_2CO_3$. By exposure to air or by the action of carbon dioxide on its solution, the normal carbonate is converted into the **bicarbonate**, $(NH_4)HCO_3$, which is the most stable carbonate of the series (compare $NH_4{\cdot}SH$).

Cyanogen Compounds.

Ammonium cyanide, $NH_4 \cdot CN$, is present in the ammoniacal liquors of the gas-works, but can be retained as ammonium sulphocyanide, $NH_4 \cdot CNS$ (which does not vaporise with the ammonia), or by the action of ferrous hydroxide, which converts it into ammonium ferrocyanide $(NH_4)_4FeC_6N_6$. The blue colour sometimes seen in commercial ammonium salts is due to the conversion of ammonium cyanide into ferric ferrocyanide (Prussian blue) or related compounds.

Ammonium cyanate, $NH_4 \cdot CNO$, formed by double decomposition from potassium cyanate and ammonium sulphate,

$$2KCNO + (NH_4)_2SO_4 = K_2SO_4 + 2NH_4 \cdot CNO,$$

is of interest from the fact that it is converted by ISOMERIC CHANGE into carbamide or urea (p. 459), when the solution is evaporated to dryness :

$$\underset{\text{Ammonium cyanate}}{NH_4 \cdot CNO} = \underset{\text{Carbamide or urea}}{CO(NH_2)_2}.$$

Ammonium thiocyanate, or ammonium sulphocyanide, $NH_4 \cdot CNS$, is formed by the interaction of yellow ammonium sulphide and prussic acid.

$$(NH_4)_2S_2 + HCN = NH_4 \cdot CNS + NH_4 \cdot HS$$

This action occurs in working up the ammoniacal liquors of the gas-works, which usually contain sulphuretted hydrogen and hydrogen cyanide as well as ammonia ; in presence of iron it gives rise to ferric thiocyanate, $Fe(CNS)_3$, which sometimes imparts a pink colour to commercial ammonium salts. The thiocyanate is prepared most readily from carbon disulphide and ammonia in presence of alcohol,

$$CS_2 + 4NH_3 = NH_4 \cdot CNS + (NH_4)_2S.$$

Ammonium thiocyanate is a colourless salt which is freely soluble in water. It is used in analysis for the detection of ferric iron, as $Fe(CNS)_3$ (pink coloration), for the estimation of silver by titration, when the insoluble silver salt, AgCNS, is precipitated, and for the quantitative estimation of copper as cuprous thiocyanate, CuCNS.

Other Ammonium Salts.

Ammonium sulphate, $(NH_4)_2SO_4$, is prepared industrially on a very large scale by passing ammonia from the aqueous liquor of the gas-works into sulphuric acid. Large quantities of the salt are also produced by similar methods as a by-product in the manufacture of coke. The annual production from these two sources in Great Britain is about one-third of a million tons.

Ammonium sulphate is readily soluble in water, but separates without water of crystallisation. The anhydrous salt is isomorphous with potassium sulphate. When crystallised from sulphuric acid or

when partially decomposed by heat, it yields the **acid sulphate,** $(NH_4)HSO_4$.

Ammonium sulphate is used very largely as a fertiliser in agriculture, and is the source from which ammonia and other ammonium salts are commonly prepared.

Ammonium nitrate, $NH_4 \cdot NO_3$.

Ammonium nitrate can be prepared by neutralising nitric acid (*e.g.*, waste nitric acid recovered from nitration, p. 395) with ammonia,

$$HNO_3 + NH_3 = NH_4 \cdot NO_3.$$

It can also be prepared by the action of ammonia and carbon dioxide on calcium nitrate (p. 638),

$$Ca(NO_3)_2 + 2NH_3 + CO_2 + H_2O = CaCO_3 + 2NH_4 \cdot NO_3,$$

or by double decomposition from sodium nitrate, the sodium being

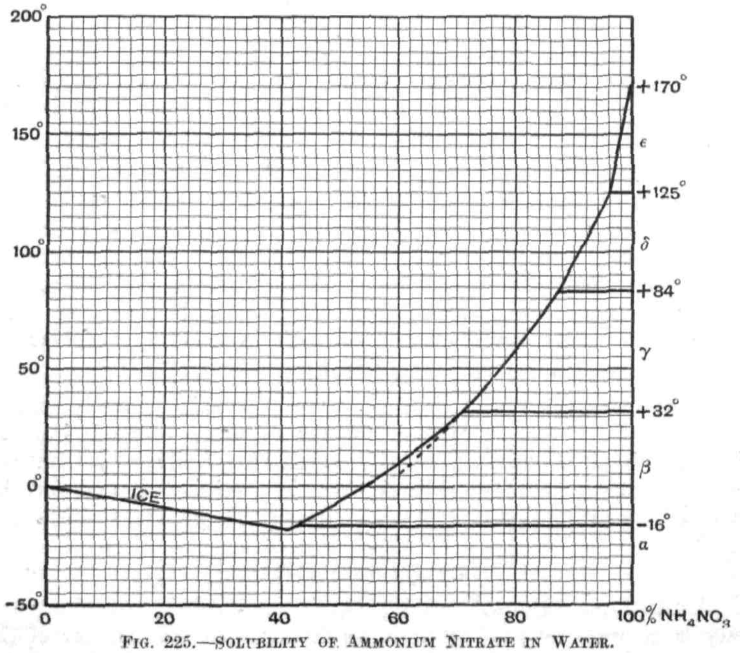


FIG. 225.—SOLUBILITY OF AMMONIUM NITRATE IN WATER.

precipitated either in the form of sodium bicarbonate in the Solvay plant, or as sodium sulphate :

$$NH_3 + CO_2 + H_2O + NaNO_3 = NaHCO_3 + NH_4 \cdot NO_3,$$
$$(NH_4)_2SO_4 + 2NaNO_3 = Na_2SO_4 + 2NH_4 \cdot NO_3.$$

The last process has the advantage that the ammonium salt and the nitrate are used in the most convenient and cheapest form.

Ammonium nitrate sublimes in glistening crystals when heated in a vacuum at 120°. It melts at 169·6° and during cooling undergoes changes of crystalline form at 125°, 84°, and 32°; there is also another form of the salt which is stable below − 16°; the salt is, therefore, PENTAMORPHOUS. The form which is stable between 32° and 84° is isomorphous with the ordinary form of potassium nitrate.

Ammonium nitrate is freely soluble in water, which dissolves 11 times its weight of the salt at 100° and 1·2 times at 0°. The solubilities of the various forms of ammonium nitrate are shown in Fig. 225 by a series of lines which intersect one another in just the same way as when a series of hydrates is formed.

The molten salt decomposes at a temperature of about 220°, or at a lower temperature when chlorides are present, giving nitrous oxide and water as the products,

$$NH_4 \cdot NO_3 = N_2O + 2H_2O.$$

This decomposition takes place explosively when the nitrate is dropped on to a hot plate, and under exceptional conditions the salt can detonate with very great violence. Mixtures of ammonium nitrate with oxidisable substances such as charcoal and aluminium, or with explosives containing an excess of oxidisable material, are used extensively as blasting explosives and for military service, thus DYNAMITE is now commonly prepared by absorbing nitroglycerine, $C_3H_5(NO_3)_3$, in ammonium nitrate instead of in kieselguhr.

Ammonium nitrite, $NH_4 \cdot NO_2$.

This salt can be prepared by double decomposition from ammonium chloride and sodium nitrite,

$$NH_4Cl + NaNO_2 = NH_4 \cdot NO_2 + NaCl;$$

the concentrated solutions is evaporated in a vacuum at 60°, and the solid residue is then sublimed at 80°. The product is a colourless, deliquescent salt which sublimes slowly at atmospheric temperatures and vaporises in a current of steam.

When a mixture of ammonium sulphate and sodium nitrite is heated, it decomposes with formation of nitrogen and water,

$$NH_4 \cdot NO_2 = N_2 + 2H_2O.$$

This decomposition can be used to prepare "chemical nitrogen" (differing from "atmospheric nitrogen" in the absence of argon, etc.), but is liable to proceed with explosive violence.

The pure salt does not explode on heating; ammonium nitrite has, however, most of the typical characteristics of a high explosive, since it contains both hydrogen and oxygen (in the right proportions to form water) in a somewhat unstable molecule, and with no other element but nitrogen present.

Ammonium nitrite has also been prepared by the action of oxides of nitrogen on ammonium carbonate.

Ammonium Phosphates.

Although the three phosphates

Normal ammonium phosphate, $(NH_4)_3PO_4$,
Diammonium hydrogen phosphate, $(NH_4)_2HPO_4$,
Ammonium dihydrogen phosphate, $(NH_4)H_2PO_4$,

have been prepared, the only important salt of this group is **ammonium sodium hydrogen phosphate**, $(NH_4)NaHPO_4,4H_2O$, or MICROCOSMIC SALT (Greek, μικρός, small, κόσμος, the world). This salt is prepared by double decomposition from sodium and ammonium phosphates,

$$Na_2HPO_4 + (NH_4)_2HPO_4 = 2(NH_4)NaHPO_4.$$

When heated, it decomposes first into sodium dihydrogen phosphate and then into sodium metaphosphate,

$$Na(NH_4)HPO_4 = NaH_2PO_4 + NH_3,$$
$$NaH_2PO_4 = NaPO_3 + H_2O.$$

The glassy product is used in analysis in much the same way as the borax bead; it gives a series of characteristic colours when combined with metallic oxides, whilst silica remains undissolved.

Detection and Estimation of Ammonium Salts.

Ammonium salts can be detected by precipitation as **ammonium platinichloride**, $(NH_4)_2PtCl_6$. They can be detected and estimated by the liberation of ammonia from them (compare p. 884), *e.g.*,

$$NH_4Cl + KOH = KCl + NH_3 + H_2O$$
$$2NH_4Cl + MgO = MgCl_2 + 2NH_3 + H_2O.$$

Minute traces of ammonia are detected and estimated by means of NESSLER'S REAGENT (p. 884).

LITHIUM, RUBIDIUM, AND CÆSIUM.

3. Lithium, Li = 6·94.

(*a*) *Occurrence.*—Lithium is much less abundant than sodium and potassium, and its properties need only be referred to briefly. Although a rare element, it is very widely diffused in nature, and by means of its striking spectrum its presence can be recognised in the ashes of beetroot, tobacco, and tea, as well as in many mineral waters and many forms of dust. It was discovered by Arfvedson in 1818 in the mineral PETALITE, a **lithium alumino-tetrasilicate,** $LiAlSi_4O_{10}$ (compare felspar, $KAlSi_3O_8$, leucite, $KAlSi_2O_6$, and nephelite, $[Na,K]AlSiO_4$), containing from 2·6 to 4·2 per cent. of Li_2O. It is also found in LEPIDOLITE,

$(AlF_2)Li_3Si_3O_8$, a mica with a violet tint which is probably due to manganese.

(*b*) *Metallic Lithium.*—The metal can be isolated by electrolysing the molten chloride, LiCl, and resembles sodium and potassium in its general properties. It is one of the lightest solids known, its density being only 0·53.

(*c*) *Chemical Properties.*—Like the first members of some other groups, lithium exhibits properties which are somewhat abnormal in comparison with those of the later members of the group; in particular, many of its properties resemble those of the elements of the alkaline earths which form the next group.* Thus, the metal burns in air with a dazzling white flame like magnesium, and decomposes water much more slowly than sodium. It burns in hydrogen to form **lithium hydride,** LiH, a white powder which is decomposed by water, liberating hydrogen; the ease of preparation of this compound may be compared with that of calcium hydride, CaH_2. Lithium also shares with magnesium and calcium the property of absorbing nitrogen, forming a stable **lithium nitride,** Li_3N, the action being so energetic that the mass may become incandescent; the product is decomposed by water, giving ammonia and lithium hydroxide:

$$Li_3N + 3H_2O = NH_3 + 3LiOH.$$

Lithium hydroxide, LiOH, is a caustic alkali, but requires eight times its weight of water to dissolve it, whilst sodium hydroxide will dissolve in an equal weight, and potassium hydroxide in half its weight of water; its sparing solubility illustrates the tendency of lithium compounds to resemble those of the calcium group. **Lithium carbonate,** Li_2CO_3, shows this tendency in a still more striking form, as it only dissolves to the extent of 1·4 per cent. in water and separates from it in an anhydrous form. Again, **lithium phosphate,** $Li_3PO_4,\frac{1}{2}H_2O$, like calcium phosphate, is almost insoluble in water.

Lithium chloride, LiCl, on the other hand, differs from the other chlorides of the family, NaCl, KCl, etc., in that it is deliquescent and freely soluble in water, which dissolves almost its own weight of the salt; moreover, it combines with water to form a series of hydrates with one, two, or three molecules of water, whereas the other chlorides of the group are always anhydrous except common salt, which forms a hydrate, $NaCl,2H_2O$, only stable below the freezing-point of water. Even this contrast is, however, in the direction of a closer resemblance to magnesium and calcium chlorides, which show these properties in a still more pronounced form.

(*d*) *Uses.*—The fact that lithium urate is soluble in water has led to the idea that lithium salts may be of value in the treatment of gout, by dissolving out uric acid.

* Compare the close resemblance between beryllium and aluminium (p. 649), boron and silicon (p. 482), oxygen and chlorine (p. 274).

37. Rubidium, Rb = 85·45, and **55. Cæsium,** Cs = 132·81.

(*a*) *Occurrence.*—These metals were discovered by Bunsen in 1860 and 1861, by the aid of the spectroscope, in certain German mineral waters, in which they are present to a minute extent. They are found, with potassium, in saline waters, in the carnallite of the Stassfurt salt beds, in the ashes of plants, and in the salts obtained by fermenting and calcining beet-sugar residues. The best source both for rubidium and cæsium is the saline residue left from the preparation of lithium salts from the minerals PETALITE and LEPIDOLITE, which may contain perhaps ¼ per cent. of Rb_2O and Cs_2O.

(*b*) *Properties.*—These two metals resemble sodium and potassium very closely. Attention may, however, be directed to the very low melting-point of cæsium (28°), to its much higher density (1·88), and to the fact that it is the most electropositive of the elements, its hydroxide being the strongest of the alkalies. The compounds of these elements resemble those of sodium and potassium. The **platinichlorides** and **perchlorates** of rubidium and cæsium are, however, even less soluble than those of potassium, and there is a marked tendency for both rubidium and cæsium to form **perhalogen compounds** containing several halogen atoms, of the same general type as potassium tri-iodide, KI_3, for example,

$RbCl_2Br$	$RbCl_2I$	$RbCl_4I$
$RbClBr_2$	$RbClBrI$	
$RbBr_3$	$RbBr_2I$	
	RbI_3	
$CsBr_3$	CsI_3	$CsCl_4I$
$CsBr_5$	CsI_5	

CHAPTER XXXIII

METALS OF THE ALKALINE EARTHS

Atomic Number.	*Element.*	*Symbol.*		*Atomic Weight.*
4	Beryllium*	Be	=	9·1
12	Magnesium	Mg	=	24·32
20	Calcium	Ca	=	40·07
38	Strontium	Sr	=	87·63
56	Barium	Ba	=	137·37
88	Radium	Ra	=	226·4

GENERAL PROPERTIES OF THE GROUP.

Physical Properties.

The elements of this group follow immediately after the metals of the alkalies in the periodic classification of the elements. They are all well-defined metals, although only magnesium is sufficiently cheap and stable to be used largely for constructional work as a light alloy with aluminium and copper. The physical constants of the elements are shown in the following table.

TABLE 70.—PHYSICAL PROPERTIES OF THE METALS OF THE GROUP OF ALKALINE EARTHS.

	Density.	*Melting-point.*	*Boiling-point.*
Be . .	1·9	Below 1000°	?
Mg . .	1·75	650	1120°
Ca . .	1·55	800	?
Sr . .	2·55	About 800	?
Ba . .	3·78	850	Can be sublimed.

The elements are all " light metals," although not so light as the metals of the alkalies ; thus calcium and magnesium, the two lightest metals of this group, are similar in density to rubidium and cæsium, the two heaviest of the alkali-metals, whilst the density of barium rises to nearly 4. There is a still stronger contrast in the melting-points and boiling-points of the two series, since none of these metals melts below a red heat, and none of them can be vaporised with the relative ease of the alkali-metals.

* Or Glucinum, Gl = 9·1.

Calcium, strontium, and barium salts impart characteristic colours to the flame as follows :

Element.	*Flame-colour.*
Calcium	Orange-red
Strontium	Deep red
Barium	Light green

The spectra are far more complicated than those of the alkalies and it would be difficult, if not impossible, to use them as sources of monochromatic light ; the nitrates are, however, used extensively in pyrotechnics. Magnesium does not give a flame spectrum, perhaps because its chloride, nitrate, etc., are so easily decomposed, whilst its oxide is far too refractory to be vaporised in a flame.

Chemical Properties.

(*a*) *Valency.*—As in the case of the elements of the alkalies, fixity of valency is an outstanding characteristic of this group. The elements are all bivalent, giving hydrides, oxides, and chlorides of the formulæ MH_2, MO, MCl_2, and nitrates, sulphates, and phosphates of the formulæ $M(NO_3)_2$, MSO_4, and $M_3(PO_4)_2$. Apart from the peroxides, such as barium peroxide, BaO_2, compounds of abnormal valency are so rare as to be almost unknown ; even in the peroxides the valency of the metal may be quite normal, as in the formula $Ba\left<\begin{matrix}O\\ |\\ O\end{matrix}\right.$, where barium and oxygen are both shown as bivalent elements.

(*b*) *Combination with Non-metals.*—The four elements magnesium, calcium, strontium, and barium are commonly known as the metals of the alkaline earths. They form a natural group of elements, their oxides, the " alkaline earths," such as magnesia and lime, being intermediate in properties between the alkalies, such as caustic soda and caustic potash, and the earths, of which alumina may be taken as the type. Although less active than the metals of the alkalies, these four metals show great chemical activity ; thus, they are easily burnt, are capable of decomposing water either at the ordinary temperature or when heated, and share with lithium the property of combining directly with nitrogen as well as with carbon,* hydrogen,* oxygen, and chlorine. Their ready combination with carbon makes it difficult or impossible to prepare calcium, strontium, or barium by reduction from their oxides, so that reduction of the chlorides by sodium or by electrolysis has generally been used instead.

(*c*) *Solubility of Salts.*—Whilst the salts of the alkalies dissolve freely in water, many of the salts of the alkaline earths dissolve only to a

* Except magnesium, which does not form a carbide or hydride ; for the properties of beryllium, which resembles aluminium rather than the metals of the alkaline earths, see p. 649 below ; for those of radium, see p. 904.

slight extent in water. Amongst these insoluble or sparingly soluble salts are

the oxides, MgO, CaO ;
the carbonates, $MgCO_3$, $CaCO_3$, $SrCO_3$, $BaCO_3$;
the sulphates, $CaSO_4$, $SrSO_4$, $BaSO_4$; and
the phosphates, $Mg_3(PO_4)_2$, $Ca_3(PO_4)_2$, $Sr_3(PO_4)_2$, $Ba_3(PO_4)_2$;

magnesium sulphate, on the other hand, dissolves readily in water. The chlorides and nitrates are also freely soluble in water, and in the case of magnesium and calcium are deliquescent. The sulphides (unlike the oxides) are also soluble, whilst the solubility of the chromates resembles that of the sulphates, becoming less and less as the atomic weight increases. The oxides and hydroxides, on the other hand, which are at first insoluble in water, become increasingly soluble and tend to separate with water of crystallisation as the atomic weight increases.

12. MAGNESIUM. Mg = 24·32.

Occurrence of Magnesium.

Magnesium does not occur in the free state, but magnesium oxide, MgO, is widely distributed in combination with silica and with carbon dioxide, and is only less common than silica, alumina, oxides of iron, and lime ; thus, igneous rocks contain nearly 4 per cent. of magnesia as compared with 5 per cent. of lime, 6 per cent. of oxides of iron, and 15 per cent. of alumina. In igneous rocks, magnesium silicates are associated with ferrous silicates in ferromagnesian minerals, but in sedimentary rocks magnesium and calcium carbonates are commonly associated together.

(*a*) *Magnesium Silicates.*—The principal magnesium silicates are :

(i) **Magnesium orthosilicate,** Mg_2SiO_4, the principal constituent of OLIVINE (Fig. 198, p. 509).

(ii) **Magnesium metasilicate,** $MgSiO_3$, the principal constituent of HORNBLENDE and AUGITE (Fig. 199, p. 509).

The products of hydrolysis of these rocks include SERPENTINE and TALC.

$$\underset{\text{Olivine}}{2Mg_2SiO_4} + 2H_2O + CO_2 = \underset{\text{Serpentine}}{H_4Mg_3Si_2O_9} + MgCO_3$$

$$\underset{\text{Hornblende}}{4MgSiO_3} + H_2O + CO_2 = \underset{\text{Talc}}{H_2Mg_3(SiO_3)_4} + MgCO_3.$$

The formulæ of these and some related magnesium silicates may be set out thus :

Serpentine, $H_4Mg_3Si_2O_9$, compare kaolinite, $H_4Al_2Si_2O_9$
Meerschaum, $H_4Mg_2Si_3O_{10}$ or $H_2SiO_3,2MgSiO_3,H_2O$
Talc, $H_2Mg_3Si_4O_{12}$ or $H_2SiO_3,3MgSiO_3$
Asbestos, $CaMg_3Si_4O_{12}$ or $CaSiO_3,3MgSiO_3$.

A fibrous form of serpentine is also used, under the name of asbestos,

for insulating and fire-resisting fabrics, although the typical ASBESTOS is a calcium magnesium silicate as set out above.

(*b*) *Magnesium Carbonates.*—Magnesium is dissolved out from ferro-magnesian silicates as **magnesium bicarbonate,** $Mg(CO_3H)_2$, a compound which is more stable than calcium bicarbonate, but decomposes in a similar manner, giving rise to deposits of **magnesium carbonate** or MAGNESITE, $MgCO_3$.

DOLOMITE is a **magnesium calcium carbonate,** $MgCaC_2O_6$, analogous to diopside, $MgCaSi_2O_6$ (Fig. 227), which is found in enormous quantities. It is believed to have been produced by the action of the soluble magnesium salts of sea-water upon calcium carbonate originally precipitated by marine organisms.

(*c*) *Magnesium Sulphate and Chloride.*—Magnesium sulphate is freely soluble in water and remains in solution where calcium salts are precipitated as calcium sulphate, or even as calcium carbonate. Magnesium salts therefore accumulate in the mother-liquors of sea-water, which are known as BITTERN, from the bitter taste which the magnesium salts impart to it. Magnesium salts are also found in certain salt-beds, where they have been carried down in combination with gypsum as POLYHALITE, $2CaSO_4,Mg(SO_4K)_2,2H_2O$, or crystallised from the mother-liquors as

KIESERITE, $MgSO_4,H_2O$,
SCHÖNITE, $Mg(SO_4K)_2,6H_2O$,
KAINITE, $MgSO_4,KCl,3H_2O$, or
CARNALLITE, $MgCl_2,KCl,6H_2O$.

Magnesia and Lime as Alkaline Earths.

Magnesia, MgO, and lime, CaO, have been associated together very closely as the two typical alkaline earths ever since Black in 1755 discovered the composition of chalk, and explained the burning of chalk to lime in the course of an investigation of the analogous behaviour and properties of magnesia. The insoluble carbonates, $CaCO_3$ and $MgCO_3$, occur together in nature as DOLOMITE in immense geological formations, whilst the soluble salts are commonly associated in " hard waters " and in sea-water. In some respects magnesia is perhaps an even better type of an ALKALINE EARTH than lime, since it is almost insoluble in water, and therefore a more representative " earth," although it still imparts to water an alkaline reaction.

Relationship of Magnesium to Zinc.

In addition to its relationship to calcium, magnesium shows several important points of resemblance to zinc, a bivalent element in the central portion of the first long period of the periodic classification.

(*a*) The solubility of **magnesium sulphate,** $MgSO_4,7H_2O$, gives to this salt a marked similarity to zinc sulphate, $ZnSO_4,7H_2O$, although

an increase in the solubility of the sulphates with decreasing molecular weight is already indicated in the sequence $BaSO_4$, $SrSO_4$, $CaSO_4,2H_2O$.

(*b*) Magnesium also resembles zinc rather than calcium, strontium, and barium in its tendency to form **basic carbonates** when precipitated from solution ; the growing instability of the carbonates as the atomic weight of the metal diminishes is, however, already seen in the effect of heat on $BaCO_3$, $SrCO_3$, $CaCO_3$, and $MgCO_3$, and it is perhaps not surprising that in contact with water magnesium should be precipitated as a basic rather than as a normal carbonate.

(*c*) At a time when metallic calcium was almost unknown, it was natural to compare the properties of **metallic magnesium** with those of metallic zinc and to think of calcium as an element of a different type. This analogy has, however, lost much of its significance since calcium also became a commercial metal ; thus the preparation of calcium by electrolysis and its physical properties are very similar to those of magnesium, whilst there is a marked contrast between the preparation and properties of magnesium and those of the metals zinc and cadmium as prepared by reduction of the oxides with carbon (p. 869).

The points of resemblance between magnesium and zinc are of value in considering the properties of the two elements, but are scarcely sufficient to justify the separation of magnesium from the metals of the alkaline earths and its inclusion in the same group as zinc. In particular, it may be noted that zinc, cadmium, and mercury, lying in the troughs of the atomic volume curve, are typical industrial metals, derived (like copper and lead) mainly from sulphide ores which have been deposited in narrow mineral veins, probably from solutions brought up from great depths. Magnesium and calcium, on the other hand, are not found as sulphides, but as sulphates, and their carbonates are typical rock-forming minerals which occur in such immense quantities that there can never be any question of a scarcity of either of these elements, such as that which causes the constant fluctuations in the price of metals such as zinc and lead, which are derived from vein-minerals.

Preparation of Metallic Magnesium.

Magnesium cannot be prepared by reducing the oxide with carbon or with hydrogen. It was formerly manufactured by heating fused carnallite, $KMgCl_3$, with metallic sodium, and purified by distillation,

$$KMgCl_3 + 2Na = 2NaCl + KCl + Mg.$$

This method has now been superseded by an electrolytic process, in which fused carnallite (which melts below 700°) is electrolysed in an iron pot, which serves as a cathode, whilst the anode is a carbon rod surrounded by a porcelain tube to lead off the chlorine (compare the preparation of sodium, p. 213),

$$MgCl_2 = Mg + Cl_2.$$

The magnesium which separates at the *bottom* of the pot is remelted with carnallite, ladled off, and cast into ingots. In another process a mixture of fluorides is used, *e.g.*, MgF_2, BaF_2, and NaF, the procedure being modelled on that used in the manufacture of aluminium (Fig. 241, p. 654).

Properties of Metallic Magnesium.

Magnesium is a brilliant white metal which can be drawn into wire and rolled into ribbon. Its density, 1·75, is below that of aluminium, 2·70. It forms a series of useful alloys with aluminium, *e.g.*, MAGNALIUM (p. 656), which are less dense than aluminium and give castings that can be worked like brass; but for equal weights these are inferior to the stronger alloys of aluminium.

Magnesium burns in air with a brilliant white light, rich in actinic rays; it is therefore used in the manufacture of star-shells for military and naval service; magnesium powder, mixed with potassium chlorate, is also used as a flash-light in photography. When burnt in air, magnesium forms both **magnesium oxide,** MgO, and **magnesium nitride,** Mg_3N_2, a greenish-yellow amorphous mass, which is decomposed readily by water, liberating ammonia,

$$Mg_3N_2 + 3H_2O = 3MgO + 2NH_3;$$

thus, when magnesium powder is heated in a crucible with a small hole in the lid, both oxygen and nitrogen are absorbed. Magnesium nitride can also be prepared by heating magnesium in nitrogen, and this action has been used to separate nitrogen from the gases of the argon group.

Magnesium is not affected by dry air at atmospheric temperatures, nor by water from which all carbon dioxide has been expelled; but when this gas is present the metal is corroded by moist air, and is attacked rapidly by water. Hydrogen is evolved in this action and the magnesium passes into solution as **magnesium hydroxycarbonate,** $HO{\cdot}Mg{\cdot}CO_3H$,

$$Mg + H_2CO_3 + H_2O = HO{\cdot}Mg{\cdot}CO_3H + H_2,$$

or, when an excess of carbon dioxide is present, as **magnesium bicarbonate,** $Mg(CO_3H)_2$,

$$Mg + 2H_2CO_3 = Mg(CO_3H)_2 + H_2.$$

Hydrogen is also evolved slowly when magnesium is boiled with water,

$$Mg + 2H_2O = Mg(OH)_2 + H_2;$$

a similar, but more rapid, action occurs when superheated steam is passed over the hot metal, which then bursts into flame. Magnesium will also decompose carbon dioxide; thus, if ignited in air the metal will continue to burn when plunged into carbon dioxide, magnesia being formed and carbon deposited from the gas,

$$2Mg + CO_2 = 2MgO + C.$$

At high temperatures, magnesium is a powerful reducing agent and has been used in preparing elements such as silicon and boron from their refractory oxides.

COMPOUNDS OF MAGNESIUM.

Oxides and Hydroxide.

Magnesium oxide, MgO, is formed when the metal is burnt in oxygen, and is prepared on a large scale by igniting magnesite, $MgCO_3$,

$$MgCO_3 = MgO + CO_2.$$

This action proceeds readily under a very gentle heat, and affords a convenient method of generating small quantities of pure carbon dioxide, *e.g.*, for use in analysis. Unlike lime, the product does not slake. It is almost insoluble in water, but imparts to it an alkaline reaction.

Magnesium oxide is a remarkably stable and refractory material, its melting-point being about 2800° ; it is therefore used in constructing furnaces for metallurgical operations, and in the manufacture of crucibles and cupels.

Magnesium oxide, prepared by igniting the basic carbonate " magnesia alba " (p. 618), is used in medicine as LIGHT or HEAVY MAGNESIA, according to the type of carbonate from which it is made.

Magnesium hydroxide, $Mg(OH)_2$, is precipitated as a gelatinous mass on adding a solution of potassium or sodium hydroxide to a soluble salt of magnesium ; it is soluble in solutions of ammonium chloride, perhaps in the form of the double salt, $(NH_4)MgCl_3$ (see below, p. 621), and is, therefore, not precipitated by ammonia in presence of ammonium salts. It is easily converted into the oxide by heating it.

Magnesium peroxide, MgO_2, has been prepared in solution by adding sodium or barium peroxide to a concentrated solution of magnesium sulphate or chloride and has been used as an antiseptic under the name of NOVOZONE.

Carbonates of Magnesium.

(*a*) **Magnesium carbonate,** $MgCO_3$, occurs naturally as MAGNESITE, either in well-defined rhombohedral crystals, isomorphous with calcite, or in large amorphous rock masses as in the Grecian island of Eubœa. This carbonate is probably a polymeric form, $(MgCO_3)_n$, since it is insoluble in water and is not affected by boiling with dilute alkali carbonates. The magnesium carbonate, $MgCO_3$, obtained by heating **magnesium ammonium carbonate,** $Mg(CO_3NH_4)_2$ (p. 619), in a stream of dry air at 130–140°, differs entirely from magnesite in its properties, since it is hygroscopic and when moistened with water sets to a mass of crystals of the **hydroxycarbonate,** $HO{\cdot}Mg{\cdot}CO_3H,2H_2O$ (p. 619).

It also dissolves in water to the extent of about 3 grams of $MgCO_3$ per litre; but the solution soon deposits crystals of the hydroxycarbonate.

(*b*) **Magnesium bicarbonate,** $Mg(CO_3H)_2$, is formed when carbon dioxide is passed through water in which magnesite is suspended. The magnesium carbonate dissolves slowly and, if a pressure of 1 atmosphere of carbon dioxide be maintained, finally gives a solution known as FLUID MAGNESIA, containing about 26 grams of $MgCO_3$ per litre in the form of the bicarbonate, $Mg(CO_3H)_2$. When the pressure of carbon dioxide above the solution is diminished, carbon dioxide is lost and some of the bicarbonate is decomposed according to the equation

$$Mg(CO_3H)_2 \quad = \quad HO{\cdot}Mg{\cdot}CO_3H \quad + \quad CO_2.$$

A similar decomposition, followed by a further loss of water and of carbon dioxide, is brought about by boiling the solution (see below).

(*c*) **Magnesium hydroxycarbonate,** $HO{\cdot}Mg{\cdot}CO_3H$.—When a solution of the bicarbonate, $Mg(CO_3H)_2$, is heated at 50°, well-formed prisms separate, which have the empirical composition $MgCO_3,3H_2O$, but are really a **dihydrated magnesium hydroxycarbonate,** $HO{\cdot}Mg{\cdot}CO_3H,2H_2O$, formed as follows:

$$Mg\left\langle\begin{array}{l}CO_3H\\ CO_3H\end{array}\right. + \quad 2H_2O \quad = \quad Mg\left\langle\begin{array}{l}OH\\ CO_3H\end{array}\right. ,\ 2H_2O \quad + \quad CO_2.$$

When these crystals are heated at 100° after drying in the air, they lose water and give the **anhydrous hydroxycarbonate,** $HO{\cdot}Mg{\cdot}CO_3H$, which is also crystalline. On attempting to drive off the last molecule of water by heating, *e.g.*, to 125°, carbon dioxide is expelled, and magnesium hydroxide is formed:

$$Mg\left\langle\begin{array}{l}OH\\ CO_3H\end{array}\right. \quad = \quad Mg\left\langle\begin{array}{l}OH\\ OH\end{array}\right. \quad + \quad CO_2.$$

In the same way, when a solution of magnesium bicarbonate is heated, the crystals of dihydrated magnesium hydroxycarbonate, $HO{\cdot}Mg{\cdot}CO_3H,2H_2O$, which separate at 50°, lose water above this temperature and are converted into the anhydrous compound $HO{\cdot}Mg{\cdot}CO_2H$; finally, when the solution is boiled, some of the hydroxycarbonate is converted into the hydroxide according to the equation

$$HO{\cdot}Mg{\cdot}CO_3H \quad = \quad Mg(OH)_2 \quad + \quad CO_2.$$

The precipitate obtained by boiling a solution of magnesium bicarbonate therefore consists of a mixture of crystals of $HO{\cdot}Mg{\cdot}CO_3H,2H_2O$ and $HO{\cdot}Mg{\cdot}CO_3H$ with $Mg(OH)_2$, the proportions of these constituents varying with the length of time of boiling, as the decomposition is progressive.

A similar mixture, containing a large proportion of the hydroxycarbonate, is used in pharmacy under the name of MAGNESIA ALBA.

HEAVY MAGNESIA is prepared by boiling a solution of Epsom salts with sodium carbonate, washing and drying at 100°, whilst LIGHT MAGNESIA is formed by precipitating from cold dilute solutions, and drying at 100°. Mixtures of this kind, which are generally described as BASIC CARBONATES, are always precipitated when an alkaline carbonate, for example sodium carbonate, is added to a solution of a magnesium salt. These "basic carbonates" have generally been regarded as formed by the action of water on the normal carbonate, $MgCO_3$, which was considered to be the first product of the action, as in the case of the calcium, strontium, and barium salts which yield only the normal carbonate under these conditions ; it has been shown, however, that they are formed by the action of water on a double carbonate which is the primary product of the action, *e.g.*,

$$MgSO_4 + 2Na_2CO_3 = Mg(CO_3Na)_2 + Na_2SO_4.$$

(*d*) **Double carbonates** of magnesium with sodium and potassium are formed when magnesium carbonate is dissolved in a concentrated solution of sodium or potassium carbonate. The crystalline products have the composition

$$MgCO_3,Na_2CO_3 \text{ and } MgCO_3,K_2CO_3,4H_2O,$$

but are probably salts of magnesium bicarbonate,

$$Mg\begin{cases}CO_3Na\\CO_3Na\end{cases} \text{ and } Mg\begin{cases}CO_3K\\CO_3K\end{cases}, 4H_2O.$$

They are only stable in solution when an excess of alkali is present, so that on adding water, or on heating, they are converted into the hydroxycarbonate, $HO{\cdot}Mg{\cdot}CO_3H$, or its hydrate, and finally into the hydroxide, $Mg(OH)_2$, thus,

$$Mg\begin{cases}CO_3Na\\CO_3Na\end{cases} + H_2O = Mg\begin{cases}OH\\CO_3H\end{cases} + Na_2CO_3,$$

$$Mg\begin{cases}OH\\CO_3H\end{cases} = Mg(OH)_2 + CO_2.$$

These double carbonates are of considerable importance, and the formation of one of them, viz., $Mg\begin{cases}CO_3H\\CO_3K\end{cases}, 4H_2O$, which takes place when carbon dioxide is passed through a solution of potassium chloride in presence of magnesium carbonate, is used on a large scale in the manufacture of potassium carbonate (p. 595). The formation of a double carbonate, $Mg(CO_3NH_4)_2$, is probably responsible for the fact that magnesium, unlike calcium, strontium, and barium, is not pre-

cipitated in qualitative analysis by the addition of ammonium carbonate and ammonium chloride to solutions of its soluble salts.

The double carbonate DOLOMITE has the composition $MgCO_3,CaCO_3$, but may also be represented like the sodium and potassium salts as $Mg(CO_3)_2Ca$. Dolomite is remarkable in that although calcite, $CaCO_3$, and magnesite, $MgCO_3$, are isomorphous with one another, the crystals of dolomite are of fixed composition and must therefore be regarded as containing a double salt rather than as an isomorphous mixture. The crystals of dolomite are of a lower order of symmetry than calcite and magnesite, although the angles between the faces are similar (p. 631); they are also slightly denser than the average of the two carbonates.

Magnesium Silicates.

Magnesium orthosilicate, Mg_2SiO_4, occurs in nature as OLIVINE, whilst **magnesium metasilicate,** $MgSiO_3$, is present in AUGITE and HORNBLENDE with the isomorphous ferrous silicate, $FeSiO_3$. The pure orthosilicate melts at 1890°; the pure metasilicate melts at 1557°, with decomposition to the orthosilicate and a liquid rich in silica, but forms a stable **magnesium calcium silicate,** $MgCa(SiO_3)_2$, known as DIOPSIDE (see Figs. 226 and 227), melting-point 1380°, when melted with calcium metasilicate, melting-point 1540°.

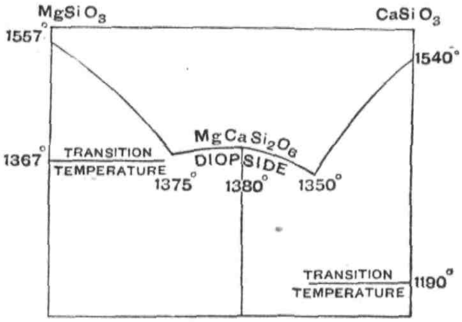


FIG. 226.—FREEZING-POINT DIAGRAM FOR MAGNESIUM AND CALCIUM SILICATES.

Magnesium metasilicate is pentamorphous. There is a high-temperature form which is stable only above 1367°; below this temperature there are four modifications, all of which are known as minerals; two of these are orthorhombic and two are monosymmetric; two are "pyroxenes" cleaving into prisms with an angle of 93°, like the monosymmetric mineral AUGITE, and two are "amphiboles" cleaving into prisms with an angle of 124°, like the monosymmetric mineral HORNBLENDE, thus,

Crystalline Form.	*Mineral.*	*Density.*	*Method of Crystallisation.*
(1) Monosymmetric pyroxene	Augite	3·192	From glass at 1300°.
(2) Orthorhombic pyroxene	Enstatite	3·175	,, ,, 1000°.
(3) Monosymmetric amphibole	Hornblende	?	From melt by rapid cooling.
(4) Orthorhombic amphibole	Anthophyllite	2·857	From overheated melt by rapid cooling in air.
(5) Glass	—	2·743	

These modifications are stable in the order of their increasing densities and tend to change into the monosymmetric pyroxene (compare augite) when heated at all temperatures below 1367°. The less stable forms are obtained as a rule by crystallising the glass at various temperatures.

Soluble Salts of Magnesium.

Magnesium chloride, $MgCl_2$, is present as the **hexahydrate,** $MgCl_2,6H_2O$, BISCHOFITE, in the upper layers of the Stassfurt salt-beds, and large quantities are produced by concentrating the mother-liquors from which potassium salts have crystallised. It separates from water in colourless crystals which are very soluble and very deliquescent; the deliquescence of common salt is indeed commonly due to the presence of magnesium chloride.

When attempts are made to dry the hexahydrate, $MgCl_2,6H_2O$, by heating it above 186°, partial decomposition occurs, hydrogen chloride being liberated and magnesium oxide formed,

$$MgCl_2,6H_2O = MgO + 2HCl + 5H_2O;$$

anhydrous magnesium chloride can, however, be prepared by heating the hexahydrate in a current of hydrogen chloride, or in a vacuum at 170°, or by igniting the double chloride, $MgCl_2,NH_4Cl,6H_2O$, or $(NH_4)MgCl_3,6H_2O$ (compare carnallite, $KMgCl_3,6H_2O$, p. 587), which loses water and then ammonium chloride when heated, leaving a residue of anhydrous magnesium chloride, $MgCl_2$. Anhydrous magnesium chloride is also obtained when magnesium is heated in a current of dry chlorine.

Magnesium chloride is also "hydrolysed" (*i.e.*, decomposed by water) to a slight extent in solution, especially at high temperatures,

$$MgCl_2 + 2H_2O \rightleftharpoons Mg(OH)_2 + 2HCl.$$

It has a strong corrosive action upon iron, since the trace of acid set free in this action is replaced by further hydrolysis as fast as it is used up by the iron. The corrosive action of sea-water in marine boilers is due mainly to the magnesium chloride which it contains.

When *dry* magnesium chloride is heated at 800° to 1000° in a current of air, magnesium oxide is formed and chlorine is liberated,

$$MgCl_2 + O = MgO + Cl_2.$$

This action has been proposed as a means of utilising the chlorine in the waste liquors of the ammonia-soda process (p. 572), by using magnesia instead of lime to liberate the ammonia.

When powdered magnesium oxide is mixed with a saturated solution of magnesium chloride, the mass sets after a short time, like plaster of Paris, probably owing to the formation of an oxychloride; the product obtained in this way, known originally as SOREL'S CEMENT, is now used on a large scale, mixed with cork or sawdust, for making floors, or as an artificial stone.

Magnesium sulphate, $MgSO_4$, occurs in the Stassfurt deposits as the **monohydrate,** KIESERITE, $MgSO_4,H_2O$, whilst the **heptahydrate** is found as EPSOMITE, or Epsom salts, $MgSO_4,7H_2O$. Magnesium sulphate is also present in sea-water and in many mineral waters. The mixed sulphate, SCHÖNITE, $MgSO_4,K_2SO_4,6H_2O$ or $Mg(SO_4K)_2,6H_2O$, occurs in the Stassfurt beds and can be separated from sea-water after the bulk of the salt has been removed. POLYHALITE, another of the Stassfurt minerals, is $2CaSO_4,Mg(SO_4K)_2,2H_2O$.

EPSOM SALTS were first discovered in a spring at Epsom in 1695 and have been used as a purgative for more than 200 years. They are now manufactured from kieserite by a process of solution and crystallisation. It is remarkable that kieserite is almost insoluble in water, but is slowly converted into Epsom salts, which dissolve readily.

Magnesium nitrate, $Mg(NO_3)_2$, is prepared by dissolving the oxide or carbonate in dilute nitric acid. It dissolves readily in water or in dilute alcohol and crystallises, with $6H_2O$, in prisms and needles which deliquesce on exposure to moist air. The hydrated salt loses water and some nitric acid when heated, forming a so-called basic nitrate.

Detection and Estimation of Magnesium.

Compounds containing magnesium, when heated with cobalt nitrate on charcoal in the blowpipe flame, give a pale pink mass. Potassium or sodium hydroxide produces a precipitate of **magnesium hydroxide** which is readily soluble in ammonium salts, such as ammonium chloride ; ammonia, therefore, does not produce a precipitate in presence of ammonium chloride. Alkaline carbonates produce a white precipitate with magnesium salts, which dissolves in an excess of the carbonate or in ammonium chloride. The most characteristic test for magnesium is to add sodium hydrogen phosphate to the solution after ammonia and ammonium chloride, when a white crystalline precipitate of **magnesium ammonium phosphate** forms on stirring or shaking :

$$MgSO_4 + NH_4{\cdot}OH + Na_2HPO_4 = MgNH_4PO_4 + Na_2SO_4 + H_2O.$$

The quantitative formation of this precipitate is made use of in estimating magnesium ; the other metals present are first removed by successive treatment with hydrogen sulphide, ammonium sulphide, and ammonium carbonate, and the magnesium is then precipitated as magnesium ammonium phosphate ; this is collected, washed, and dried, detached from the filter-paper and ignited in a platinum crucible, when it is converted into magnesium pyrophosphate, $Mg_2P_2O_7$:

$$2MgNH_4PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O.$$

The atomic weight of magnesium depends on determinations of the ratios $MgCl_2 : 2Ag$ and $MgCl_2 : 2AgCl$.

20. CALCIUM. Ca = 40·07.

Occurrence of Calcium.

Metallic calcium is not found in nature, but its oxide, which forms nearly 5 per cent. of the solid crust of the earth, is only less abundant than silica, alumina, and the oxides of iron.

(*a*) *Calcium Silicates.*—The principal calcium-compound in the igneous rocks is ANORTHITE, or lime-felspar, a **calcium alumino-silicate** of the formula $Ca(AlSiO_4)_2$. A **calcium aluminium orthosilicate,** $Ca_3Al_2(SiO_4)_3$, is also found as GARNET (Fig. 227). **Calcium metasilicate,** $CaSiO_3$, occurs as WOLLASTONITE, and as **calcium magnesium silicate** in DIOPSIDE, $CaMgSi_2O_6$ (Fig. 227).

(*b*) *Calcium Carbonate.*—By the action of water and carbon dioxide, lime is extracted from the mineral silicates in the form of **calcium bicarbonate,** $Ca(CO_3H)_2$. It may be precipitated again as **calcium carbonate,** $CaCO_3$, by the escape of carbon dioxide, or carried down by the rivers to the sea as bicarbonate, sulphate, or chloride. Calcium carbonate is there precipitated from its soluble salts by the action of living organisms, including shell-fish and corals, whilst still more minute organisms are probably responsible for the calcareous oozes; from these sources the immense natural deposits of CHALK and LIMESTONE are derived. It is remarkable that calcium carbonate is only precipitated in relatively shallow water and is not found on the floor of the deep ocean below about 3,000 fathoms.

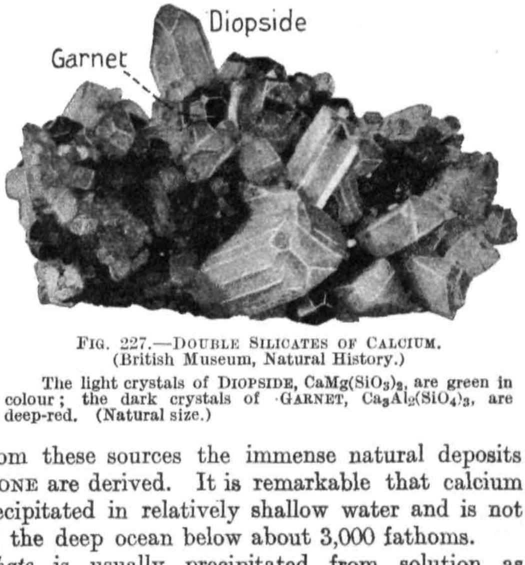


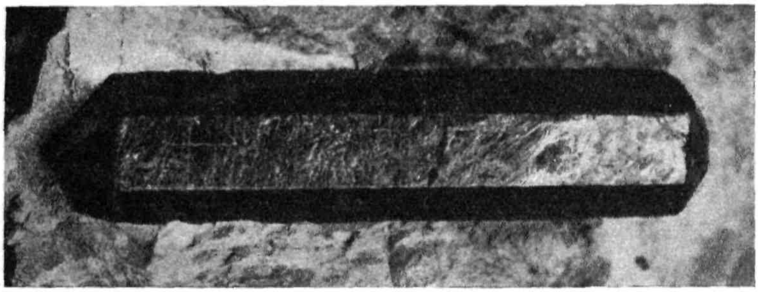
FIG. 227.—DOUBLE SILICATES OF CALCIUM. (British Museum, Natural History.)

The light crystals of DIOPSIDE, $CaMg(SiO_3)_2$, are green in colour; the dark crystals of GARNET, $Ca_3Al_2(SiO_4)_3$, are deep-red. (Natural size.)

(*c*) *Calcium Sulphate* is usually precipitated from solution as GYPSUM, $CaSO_4,2H_2O$ (Fig. 236, p. 635); but from a solution saturated with salt it separates without water of crystallisation as ANHYDRITE, $CaSO_4$, at temperatures above 30°, and usually appears in this form when associated with rock salt (compare p. 559).

(*d*) *Calcium Fluoride.*—Unlike the chloride, **calcium fluoride,** CaF_2, is insoluble in water. It is found as FLUORITE OR FLUORSPAR (Fig. 235) in mineral veins, where it appears to have been formed by the interaction of soluble calcium salts with volcanic gases or waters containing soluble fluorides or hydrofluoric acid distilled out from deep-seated rocks.

(*e*) *Calcium Phosphate* occurs in deep-seated igneous rocks as APATITE, $Ca_5(PO_4)_3F$ (Fig. 228). This compound is probably converted by the action of water and carbon dioxide into a soluble acid phosphate, *e.g.*, $CaH_4(PO_4)_2$, from which the insoluble phosphate, $Ca_3(PO_4)_2$, may be reprecipitated; or it may be absorbed by plants and converted into



× ⅓. FIG. 228.—CRYSTAL OF APATITE. (British Museum, Natural History.)

complex organic compounds which are used by animals for building up their tissues and especially the bones, of which calcium phosphate, $Ca_3(PO_4)_2$, is the principal mineral constituent. Deposits of calcium phosphate have also been formed by the action on calcareous rocks of phosphoric acid from animal excrements such as guano (p. 419.)

Preparation of Metallic Calcium.

(*a*) Metallic calcium was isolated by Davy in 1808, by electrolysing moist calcium hydroxide with a mercury cathode; metallic calcium was separated by distilling the amalgam in a current of hydrogen.

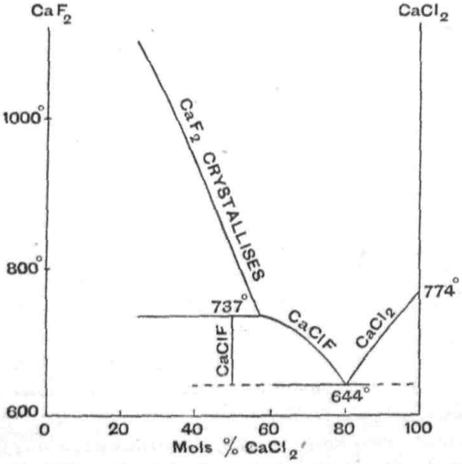


FIG. 229.—FREEZING-POINT DIAGRAM FOR CALCIUM FLUORIDE AND CALCIUM CHLORIDE.

(*b*) Moissan prepared it by heating calcium iodide with metallic sodium at a red heat,

$$CaI_2 + 2Na = Ca + 2NaI;$$

the excess of sodium was dissolved out by means of alcohol, leaving the calcium as a crystalline powder.

(*c*) Metallic calcium is now manufactured by electrolysing a fused mixture of calcium chloride and calcium fluoride at a temperature of about 700°. The product contains about

99 per cent. of calcium, the remaining 1 per cent. being made up of silicon, aluminium, and iron.

The anode is of carbon, and the cathode is an iron rod which is drawn up as the calcium is deposited upon it, in order to prevent the calcium from melting in the bath. The metal is isolated in the solid state because the liquid is not light enough to float satisfactorily on molten calcium chloride Calcium fluoride (m.p. 1378°) is added to the calcium chloride (m.p. 774°) in order to lower its freezing-point, which would otherwise be too near to that of the metal (m.p. 800°) to allow of easy electrolysis of the molten salt without also melting the metal. The eutectic mixture of the two salts freezes at 644° (Fig. 229) and thus gives a range of about 150° for the temperature of electrolysis.

Properties of Metallic Calcium.

Calcium, density 1·55, melts at about 800° and sublimes in a vacuum below its melting-point. It is a malleable metal, about as hard as tin, and can be turned in a lathe to give either a smooth bright surface or a series of screw-threads. It has a grey-white colour when freshly cut, but tarnishes gradually in moist air.

Metallic calcium combines readily with oxygen, forming the oxide CaO, and with chlorine to form the chloride $CaCl_2$. When heated in hydrogen it absorbs the gas rapidly, forming the hydride CaH_2. It also absorbs nitrogen, forming the nitride Ca_3N_2. It combines with carbon, forming the carbide CaC_2, and cannot, therefore, be prepared by reduction of the oxide with carbon.

On account of the fact that when heated it absorbs all the gases of the atmosphere, with the exception of those of the argon family, it has been used in obtaining high vacua and in the preparation of argon. It is also used instead of lime for drying " absolute " alcohol. It is used in metallurgy for improving castings by absorbing air from them, and for hardening lead.

Calcium Hydride, Nitride, and Carbide.

Calcium hydride, CaH_2, is prepared by the direct absorption of hydrogen by metallic calcium; combination takes place slowly at atmospheric temperatures and very rapidly when the solid metal is heated at 350°, or when the metal is melted; the dissociation-pressure of the hydride is 11 mm. at 780° and 705 mm. at 1027°. The hydride is a colourless or grey solid, of density 1·7, which retains the form of the metal from which it was prepared. It is decomposed rapidly by water, giving slaked lime and hydrogen:

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2;$$

in this action 42 parts of calcium hydride liberate 4 parts of hydrogen, whereas 46 parts of sodium liberate only 2 parts of hydrogen from water; calcium hydride has therefore been proposed as a convenient source of

hydrogen for balloons. Calcium hydride combines with carbon dioxide to give **calcium formate,** $Ca(O \cdot CO \cdot H)_2$:

$$CaH_2 + 2CO_2 = Ca(CO_2H)_2.$$

Calcium nitride, Ca_3N_2, is formed by heating calcium at a dull red heat in a stream of nitrogen gas. It forms brownish-yellow microscopic crystals of density 2·6. It burns in the air, forming calcium oxide and free nitrogen :

$$2Ca_3N_2 + 3O_2 = 6CaO + 2N_2.$$

It is decomposed by water, giving calcium hydroxide and ammonia,

$$Ca_3N_2 + 6H_2O = 3Ca(OH)_2 + 2NH_3,$$

and is reduced by hydrogen, forming calcium hydride and ammonia,

$$Ca_3N_2 + 6H_2 = 3CaH_2 + 2NH_3.$$

Calcium carbide, CaC_2, is prepared by heating together pure lime and carbon in an electric furnace :

$$CaO + 3C = CaC_2 + CO.$$

Commercial calcium carbide is manufactured by heating a mixture of limestone with coke or powdered coal in an electric furnace (Fig. 230). The product is drawn off and cast at a temperature of about 1800° C.

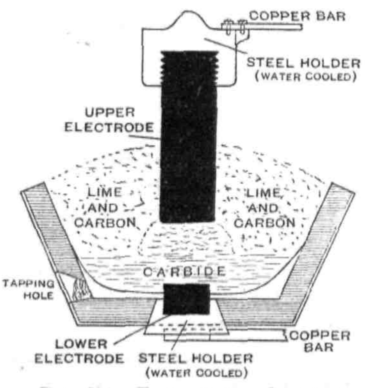


FIG. 230.—FURNACE FOR CALCIUM CARBIDE.

Pure calcium carbide forms colourless crystals of density 2·2 ; the commercial product is obtained in broken lumps of a dark colour. It is decomposed by water, forming slaked lime and acetylene :

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2 ;$$

this forms the starting point for the synthetical preparation on a large commercial scale of **aldehyde,** C_2H_4O,

$$C_2H_2 + H_2O = C_2H_4O,$$

by combination with water in presence of mercuric oxide and dilute sulphuric acid (p. 451), and of **acetic acid,** $C_2H_4O_2$, by oxidation with air in presence of manganese acetate at 25° to 40° (p. 451),

$$C_2H_4O + O = C_2H_4O_2.$$

Calcium carbide combines with nitrogen at a temperature of about 1000° to form **calcium cyanamide,** $CaCN_2$ or $CN \cdot NCa$,

$$CaC_2 + N_2 = CaCN_2 + C.$$

The fixation of nitrogen takes place more rapidly and at a lower temperature (700°) when a little chloride or fluoride is added to the

material. Calcium cyanamide liberates ammonia slowly in the soil,

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3,$$

and therefore finds application as a fertiliser. The same decomposition takes place rapidly at 180° by the action of steam under about 9 atmospheres pressure; this decomposition has been developed on a very large scale for the manufacture of ammonia and hence (by oxidation) of nitric acid (p. 390).

OXIDES, HYDROXIDE, AND CARBONATES.

Calcium Oxide or Quicklime, CaO.

(*a*) *Lime-burning.*—Pure lime is prepared by igniting calcium carbonate or calcium nitrate. The decomposition of the carbonate is a reversible action,

$$CaCO_3 \rightleftharpoons CaO + CO_2 - 42{,}000 \text{ cal.}$$

Below 500° C. the DISSOCIATION-PRESSURE of the carbonate is insignificant, but it rises to about 1/10 atmosphere at 750° and to 1 atmosphere at about 900°. In order to decompose it in a retort, or similar vessel, the carbonate must be heated nearly to 1000°, when the dissociation-pressure of the carbon dioxide is sufficient to drive back the atmosphere (compare the boiling of water). The decomposition can, however, be brought about at a much lower temperature by sweeping away the carbon dioxide in a current of air or gas (compare the evaporation of water), and this is the method used industrially for burning chalk to lime. On a large scale lime is prepared by burning LIMESTONE in a LIMEKILN either mixed with coal in a continuous process (Fig. 177, p. 456) or heated by fires burning in hearths under the kiln (Fig. 42, p. 70).

(*b*) *Physical Properties of Lime.*—Lime is a white solid of density 3·30. It is generally obtained in large lumps, corresponding in shape with the rough limestone from which it was prepared. It is very infusible and gives a brilliant white LIMELIGHT when heated in an oxy-hydrogen flame; it can, however, be melted at 2570°, and even caused to boil in an electric furnace.

(*c*) *Chemical Properties of Lime.*—Although lime combines readily with chlorine to form bleaching powder, $CaOCl_2$, with carbon dioxide to form chalk, $CaCO_3$, and with sulphur dioxide to form calcium sulphite, $CaSO_3$, when water is present, it is quite unaffected by these gases when carefully dried. In the same way, *dry* hydrogen chloride does not attack dry lime, although it is readily absorbed in presence of moisture, giving rise to calcium chloride and water,

$$CaO + 2HCl = CaCl_2 + H_2O.$$

Calcium chloride is also formed by heating quicklime strongly in a current of chlorine gas, or in the vapour of mercuric chloride,

$$2CaO + 2Cl_2 = 2CaCl_2 + O_2.$$
$$2CaO + 2HgCl_2 = 2CaCl_2 + O_2 + 2Hg.$$

(*d*) *Uses.*—Quicklime is used in the laboratory for drying alcohol, and industrially as a refractory and as a constituent of metallurgical slags; in other cases it is generally "slaked" and converted into calcium hydroxide, $Ca(OH)_2$, before being used.

(*e*) *Slaking of Lime.*—When sprinkled with water, lime becomes intensely hot, steam is given off, and the hard lumps of lime break up into a fine dry powder consisting of **calcium hydroxide,** $Ca(OH)_2$;

$$CaO + H_2O = Ca(OH)_2 + 15{,}000 \text{ cal.}$$

This process is known as SLAKING and the product as SLAKED LIME. This property is made use of in preparing lime for mixing with sand for use as MORTAR; by means of it the lime can be reduced to a powder of extreme fineness without grinding or even crushing the hard lumps of lime. Lime prepared from a fairly pure limestone, containing but little clay or magnesium carbonate, slakes readily and is described as a FAT LIME; when, however, the limestone contains a considerable proportion of magnesium carbonate, the lime slakes badly and is useless for making mortar.

(*e*) *Mortar.*—Ordinary MORTAR is made by mixing slaked lime with sand (3 or 4 parts) and water so as to give a thick paste. The SETTING of mortar depends on the loss of water from the mixture after it has been put into position between the bricks of the building in which it is used. It is possible that the setting of mortar may depend in the first instance on the excessive solubility of the very minute particles formed by slaking, giving rise to supersaturated solutions from which the excess of lime is quickly deposited. After it has set, mortar gradually absorbs carbon dioxide and the calcium hydroxide is converted into calcium carbonate. This process is known as the HARDENING of mortar; it takes place very slowly and is only complete after many years; it is, therefore, quite different from the setting of cement (p. 642).

Calcium Hydroxide or Slaked Lime, $Ca(OH)_2$.

This substance is formed on slaking lime. It is a loose white powder, of density 2·08; its low density as compared with quicklime (2·1 against 3·3) accounts for the swelling which occurs when lime is slaked. It is only slightly soluble in water, and the solubility diminishes as the temperature is raised; thus, 1 part of CaO dissolves in 780 parts of water at 15°, in 3,000 parts of water at 80°, and in 12,000 parts of water at 190°; a saturated solution, therefore, becomes turbid when boiled.

LIME-WATER, prepared by dissolving slaked lime in water, is alkaline in reaction and rapidly absorbs carbon dioxide from the air, chalk being precipitated; it is therefore commonly used as a test for carbon dioxide. Powdered slaked lime also absorbs the gas and is gradually converted into the carbonate by displacement of water,

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

MILK OF LIME is a suspension of slaked lime in water which is frequently used in chemical work on account of the limited solubility of lime.

Calcium Peroxide, CaO_2.

This compound is produced by adding a solution of hydrogen peroxide to lime-water. It is precipitated as a crystalline powder having the composition of an **octahydrate,** $CaO_2,8H_2O$; on heating this at 130° **anhydrous calcium peroxide,** CaO_2, is obtained. It is prepared on a large scale by the action of sodium peroxide on a calcium salt and is used as an antiseptic.

Calcium Carbonate and Calcium Bicarbonate.

Calcium carbonate, $CaCO_3$, is the principal form in which calcium has been segregated in nature. It is the principal constituent of the

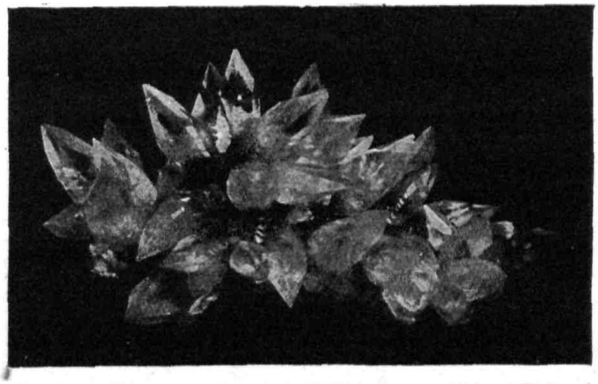


FIG. 231.—CRYSTALS OF CALCITE. (British Museum, Natural History.)

shells of marine organisms and most of it has been thrown out of solution by these organisms; thus CHALK and MOUNTAIN LIMESTONE were originally produced by the minute marine organisms known as *foraminifera*, the solid rock representing an aggregate of the skeletons of these microscopic forms. In tropical waters a still smaller organism, *Bacterium calcis*, has been found to give rise to extensive deposits of calcium carbonate in the bed of the ocean. The enormous masses of CORAL, formed by the *coral polyps*, are another form of calcium car-

bonate. MARBLE is a hard compact form of limestone which has been transformed by heat and great pressure into a mass of minute crystals.

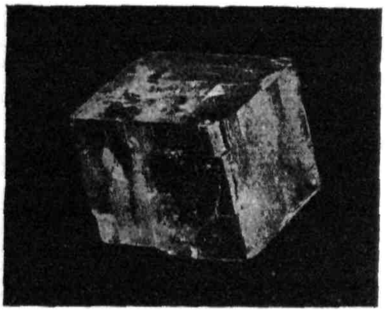


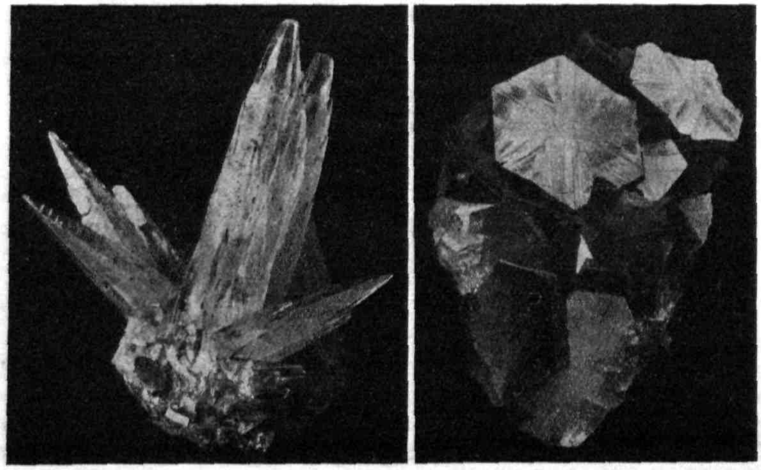
FIG. 232.—CLEAVAGE-FRAGMENT OF CALCITE.

Calcium carbonate also occurs in nature in rhombohedral crystals of density 2·71 as CALCITE, CALC-SPAR, or ICELAND SPAR (Figs. 231 and 232), and in orthorhombic crystals of density 2·93 as ARAGONITE (Fig. 233). These two forms of calcium carbonate have been deposited from solutions containing calcium bicarbonate (see below); cold solutions deposit calcite, whilst aragonite may be deposited from hot solutions; but the conditions of stability of the two forms have not been determined and there is no clear evidence of a definite transition-temperature. Calcite is isomorphous with

MAGNESITE, $MgCO_3$ SIDERITE, $FeCO_3$
CALAMINE, $ZnCO_3$ RHODOCHROSITE, $MnCO_3$.

Aragonite is isomorphous with

STRONTIANITE, $SrCO_3$ CERUSSITE, $PbCO_3$
WITHERITE, $BaCO_3$.



× ⅞. FIG. 233.—ARAGONITE. (British Museum, Natural History.)

The specimen on the left hand shows a cluster of orthorhombic crystals. The specimen on the right hand shows a characteristic twinning of the orthorhombic crystals to produce pseudo-hexagonal prisms; the twinning is made obvious by the striations on the ends of the prisms.

Calcite is also similar in crystalline form to sodium nitrate, $NaNO_3$, a soluble salt which cannot form solid solutions with calcium carbonate, but which crystallises out with parallel edges on the surface of a calcite crystal; the sum of the valencies, $Ca + C = 2 + 4 = 6$ and $Na + N = 1 + 5 = 6$, is the same in the two cases, and the identity of crystalline structure has been confirmed by examination with X-rays.

DOLOMITE, $MgCa(CO_3)_2$, resembles calcite and magnesite, but is of a lower order of symmetry in the rhombohedral system. BARYTOCALCITE, $BaCa(CO_3)_2$, is a double salt of similar type, and approximates to calcite in its cleavage, but its symmetry is degraded to that of the monosymmetric system, the angles between the cleavage faces being

	74° 6′,	74° 6′,	73° 6′
instead of	74° 55′,	74° 55′,	74° 55′.

The three orthorhombic carbonates, $SrCO_3$, $BaCO_3$, and $PbCO_3$, may occur as isomorphous constituents in rhombohedral crystals of calcite, and are therefore obviously dimorphous; conversely, zinc carbonate, $ZnCO_3$, which is usually rhombohedral, may occur as an isomorphous constituent in orthorhombic crystals of aragonite and cerussite, and must therefore also be dimorphous.

Calcium carbonate is almost insoluble in pure water, but dissolves to the extent of 1·1 grams per litre in water saturated with carbon dioxide, forming a soluble **calcium bicarbonate,** $Ca(CO_3H)_2$, as shown in the equation:

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(CO_3H)_2.$$

The solubility of calcium carbonate in water containing carbon dioxide accounts for the fact that almost all natural waters contain calcium carbonate in solution. Thus water from wells in chalk or limestone districts may contain 50 to 100 parts of $CaCO_3$ per 100,000 parts of water. On exposure to air the carbon dioxide escapes and calcium carbonate is deposited, *e.g.*, in the form of calcite or in the special forms of STALACTITES (Fig. 234) and STALAGMITES on the roofs and floors of limestone caverns. The bicarbonate is also decomposed very rapidly by boiling, carbon dioxide being evolved and calcium carbonate precipitated; when, therefore, water containing calcium bicarbonate is heated in a

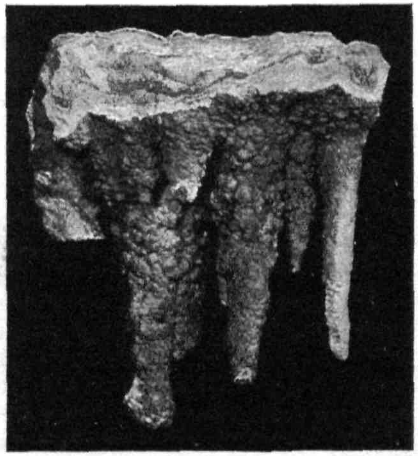


FIG. 234.—STALACTITE. (British Museum, Natural History.)

kettle or a boiler a loose powdery deposit of calcium carbonate is formed which sinks to the bottom of the vessel as BOILER MUD. When calcium sulphate is also present a hard BOILER SCALE may be formed, which is very troublesome to remove, apart from being the cause of loss of heat in steam-raising and a fertile source of boiler explosions.

Water containing calcium bicarbonate, or other soluble salts of calcium, such as calcium sulphate or calcium chloride, is described as HARD WATER. Such waters form a curd instead of a lather with soap, the soluble sodium palmitate or stearate of the soap being converted into insoluble calcium palmitate or stearate, until the whole of the calcium salts have been precipitated:

$$\underset{\text{Sodium stearate}}{2C_{17}H_{35}\cdot CO\cdot ONa} + CaCl_2 = 2NaCl + \underset{\text{Calcium stearate}}{(C_{17}H_{35}CO\cdot O)_2Ca}.$$

Hardness may also be caused by salts of magnesium and metallic salts such as ferrous bicarbonate. As the hardness of water containing calcium bicarbonate is lost after boiling, such hardness is described as TEMPORARY HARDNESS to distinguish it from that due to calcium (or magnesium) sulphate or chloride which is not diminished by this treatment and which is, therefore, called PERMANENT HARDNESS (see under calcium sulphate). Hard waters may be "softened" by precipitating the mineral salts as carbonates; thus temporary hardness can be removed by the addition of lime, and permanent hardness by the addition of sodium carbonate to the water:

$$Ca(CO_3H)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$$
$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

COMPOUNDS CONTAINING HALOGENS.

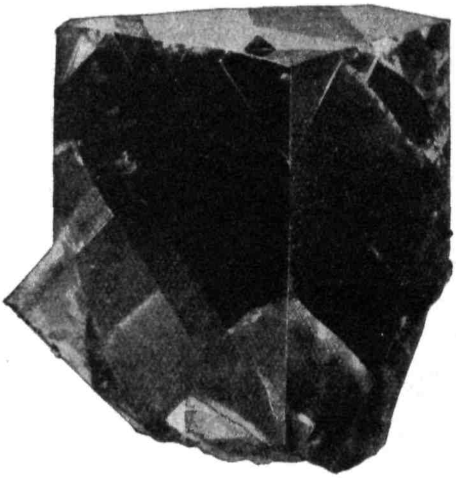
Binary Halogen-salts.

Calcium fluoride, CaF_2, or FLUORSPAR, occurs in well-formed cubical or octahedral crystals (Fig. 235) of density 3·18, *e.g.*, as a vein-material accompanying lead ores in Cumberland and Derbyshire. It is also obtained artificially in the manufacture of soda from cryolite. The mineral is of various colours, but most commonly of a blue tint, from which it derives the name of BLUE JOHN; colourless fluorspar is very rare, but is of great value for optical work, especially in the manufacture of apochromatic objectives. The blue colour of fluorspar is not due to a direct absorption of red and green rays, but to the conversion of part of the incident light into a scattered blue radiation; this transformation of light into radiation of a different colour is called FLUORESCENCE, after the mineral in which it was first observed. When viewed by transmitted light, blue fluorspar is almost colourless.

Calcium fluoride melts at 1378° and the mineral is used as a flux in metallurgical operations. Unlike the other halogen salts of calcium,

the fluoride is almost insoluble in water, differing markedly from the very soluble and deliquescent calcium chloride.

Calcium chloride, $CaCl_2$, is obtained when lime or chalk is dissolved in dilute hydrochloric acid. It is produced in immense quantities as a by-product in the manufacture of soda by the Solvay process (p. 571), and in smaller quantities in other chemical operations. Calcium chloride is very soluble in water, from which it crystallises as a **hexahydrate,** $CaCl_2,6H_2O$; this melts at 30° and deliquesces rapidly in moist air, but in the very dry air of a Canadian winter the crystals lose water and effloresce. When heated strongly the hydrate loses its water, but (unlike magnesium chloride) is not hydrolysed in the process. **Anhydrous calcium chloride,** $CaCl_2$, melts at 774°. It absorbs water readily and is used for drying gases and organic liquids such as ether. It also absorbs gaseous ammonia at atmospheric temperatures, forming a white compound, $CaCl_2,8NH_3$, which gives up its ammonia again on heating or on adding water. It also unites with alcohol to form an **alcoholate,** $CaCl_2,4C_2H_6O$.



$\times \frac{2}{3}$. FIG. 235.—CUBIC CRYSTAL OF FLUORSPAR. (British Museum, Natural History.)

Showing the characteristic twinning of the cubes, and the octahedral cleavage of the mineral, as indicated by cracks in the crystal.

Calcium bromide, $CaBr_2$, and **calcium iodide,** CaI_2, are analogous to the chloride.

Calcium Hypochlorite and Bleaching Powder.

(*a*) *Calcium Hypochlorite*, $Ca(OCl)_2$.—When chlorine is passed into well-cooled milk of lime, an action similar to that of chlorine on potassium or sodium hydroxide occurs and a solution is obtained, from which by freezing, or by "salting out" with sodium chloride, crystals of **calcium hypochlorite,** having the composition $Ca(OCl)_2,4H_2O$, can be obtained,

$$2Ca(OH)_2 + 2Cl_2 = Ca(OCl)_2 + CaCl_2 + 2H_2O.$$

(*b*) *Manufacture of Bleaching Powder.*—BLEACHING POWDER, OR

CHLORIDE OF LIME, is obtained by absorbing chlorine gas by means of *dry* slaked lime,

$$Ca(OH)_2 + Cl_2 = CaOCl_2,H_2O.$$

It is made commercially by passing chlorine into large stone chambers, containing slaked lime spread on the floor to the depth of about 4 inches; the chlorine is gradually absorbed by the lime to form bleaching powder. When tests made on the material show that it contains from 35 to 37 per cent. of "available chlorine," the slight excess of chlorine in the chamber is removed by means of a suction fan, and the product transferred to barrels. Mechanical plants arranged on the counter-current principle are also in use for making bleaching powder.

(*c*) *Properties and Uses of Bleaching Powder.*—Bleaching powder is a white powder which absorbs moisture and carbon dioxide and smells strongly of hypochlorous acid. Acids liberate chlorine from it as in the equations

$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2,$$
$$CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

Sodium bicarbonate, on the other hand, at temperatures below 0° liberates hypochlorous acid,

$$CaOCl_2 + NaHCO_3 = CaCO_3 + NaCl + HClO.$$

Solutions of hypochlorous acid prepared in this way (or from equal weights of bleaching powder and borax) and diluted to 0·25 per cent. HClO are used to irrigate infected wounds. Bleaching powder is used for bleaching cotton, linen, and paper pulp. The action, which is really one of oxidation, may be carried out either with bleaching powder alone, usually followed by exposure to air, or more rapidly by acidifying the solution.

(*d*) *Constitution of Bleaching Powder.*—Bleaching powder was at one time thought to be a mixture of calcium hypochlorite and calcium chloride formed according to the equation shown under (*a*) above; but its properties do not accord with this view, *e.g.*, it is not hygroscopic or deliquescent like calcium chloride, and calcium chloride cannot be extracted from it by means of alcohol; again, on passing carbon dioxide over bleaching powder, a larger proportion of chlorine is given off than would be obtained from a mixture of calcium chloride and calcium hypochlorite.

The properties of bleaching powder can be explained most readily by assuming that it consists largely of a compound $CaOCl_2,H_2O$, or $Cl{\cdot}Ca{\cdot}OCl,H_2O$, formed according to the equation

$$Ca(OH)_2 + Cl_2 = CaOCl_2,H_2O;$$

on keeping, however, a decomposition into calcium chloride and calcium chlorate appears to take place,

$$6CaOCl_2 = 5CaCl_2 + Ca(ClO_3)_2.$$

Practically the whole of the chlorine absorbed by the lime is set free from freshly-made bleaching-powder by dilute hydrochloric acid, and sulphuric acid acts similarly. The chlorine liberated by dilute acids is known as AVAILABLE CHLORINE and in commercial bleaching powder is 35 to 37 per cent. by weight of the material; the theoretical proportion in a compound of the composition $CaOCl_2,H_2O$ is 49 per cent., and the maximum reached experimentally is 44 per cent.

COMPOUNDS CONTAINING SULPHUR.

Calcium Sulphate, $CaSO_4$.

(*a*) *Occurrence.*—Calcium sulphate occurs naturally in two forms: (i) without water as ANHYDRITE, $CaSO_4$; (ii) with water of crystallisation as GYPSUM, $CaSO_4,2H_2O$. When the gypsum forms well-defined crystals it is known as SELENITE (Fig. 236), and when it is found in fibrous needles it is called SATIN SPAR.

FIG. 236.—LARGE CRYSTAL OF SELENITE OR GYPSUM. $\times \frac{1}{2}$.

(*b*) *Manufacture of Plaster of Paris.*—Gypsum is the raw material from which plaster of Paris, first prepared at the quarries of Montmartre near Paris, is made. Ground gypsum is heated at a temperature of 120° to 140°, when it loses three-fourths of its water of crystallisation and is converted into the **half-hydrate,** $CaSO_4,\frac{1}{2}H_2O$, or more correctly $2CaSO_4,H_2O$; this half-hydrate constitutes PLASTER OF PARIS.

(*c*) *Setting of Plaster of Paris.*—When made into a paste with a little water, plaster of Paris sets in a few minutes to a firm mass, which gradually hardens; it is therefore used largely for taking casts. The final product has the same composition, $CaSO_4,2H_2O$, as the original gypsum, but the setting is a more complex change than the mere reversal of the dehydration of the salt. Thus, when gypsum, which is a **monosymmetric dihydrate** of the formula $CaSO_4,2H_2O$, is heated, it first changes into an **orthorhombic**

dihydrate, $CaSO_4,2H_2O$, which loses water and gives an orthorhombic half-hydrate :

$$\underset{\text{Gypsum (monosymmetric)}}{CaSO_4,2H_2O} \underset{\text{SETTING}}{\overset{\text{HEATING}}{\rightleftharpoons}} \underset{\text{Orthorhombic dihydrate}}{CaSO_4,2H_2O} \underset{\text{SETTING}}{\overset{\text{HEATING}}{\rightleftharpoons}} \underset{\text{Half-hydrate (orthorhombic)}}{CaSO_4,\tfrac{1}{2}H_2O}.$$

When the plaster is mixed with water, the half-hydrate, which is soluble to the extent of about 1·2 grams per 100 c.c., passes into solution and the orthorhombic dihydrate separates as a mass of small needles until the whole of the half-hydrate has disappeared. The orthorhombic form of the dihydrate being more soluble than the monosymmetric form is then converted more slowly into ordinary gypsum. This second change is accompanied by an expansion, which is of value in ensuring that the plaster fills the mould completely. The solid product is held together by small interlacing crystals which have separated from a solution saturated with a metastable form, and therefore supersaturated as regards the stable form, of the sulphate.

(*d*) *Dimorphism of Calcium Sulphate.*—The dimorphism which is characteristic of the dihydrate, $CaSO_4,2H_2O$, appears again in the anhydrous sulphate and in its half-hydrate.

(i) **Anhydrous gypsum,** in the form of ANHYDRITE, does not set when mixed with water, and a similar product known as DEAD-BURNT GYPSUM is formed when gypsum is heated at a temperature below red heat until it has lost all its water. If, however, the half-hydrate (which can be prepared by heating gypsum in an open crucible at 100° and retains its water of crystallisation indefinitely at that temperature) be heated above 101·4°, it loses the rest of its water and is converted into a second form of anhydrous calcium sulphate, which is known as SOLUBLE ANHYDRITE, because it is appreciably soluble in water and when moistened sets like plaster of Paris, but more rapidly. Soluble anhydrite is intensely hygroscopic and when kept in a desiccator over ordinary strong sulphuric acid will take from it enough water to form the half-hydrate

$$\underset{\text{Soluble half-hydrate}}{2CaSO_4,H_2O} \underset{\text{Below } 101{\cdot}4^\circ}{\overset{\text{Above } 101{\cdot}4^\circ}{\rightleftharpoons}} \underset{\text{Soluble anhydrite}}{2CaSO_4} + H_2O.$$

(ii) The **insoluble half-hydrate,** $2CaSO_4,H_2O$, can be prepared by boiling gypsum or the soluble half-hydrate with water during about three hours. It separates frequently in steam-boilers as a hard crystalline deposit or BOILER-SCALE. It differs from the ordinary half-hydrate in being insoluble in water, and in not setting when mixed with water.

The following table gives the properties of the two series of compounds.

TABLE 71.—PROPERTIES OF CALCIUM SULPHATE.

	α Series—Sparingly soluble and slow in setting.	*β Series*—More soluble and setting rapidly.
$CaSO_4$	*Natural anhydrite.* Formed by heating gypsum to a red heat. Orthorhombic. Density 2·9.	*Soluble anhydrite.* By heating gypsum at 108°.

TABLE 71.—PROPERTIES OF CALCIUM SULPHATE (*continued*).

	α *Series*—Sparingly soluble and slow in setting.	β *Series*—More soluble and setting rapidly.
$CaSO_4,\frac{1}{2}H_2O$	*Insoluble half-hydrate.* By action of water on gypsum at 100°. Orthorhombic.	*Quick-setting half-hydrate* (plaster of Paris). By heating gypsum at 100°, or by allowing soluble anhydrite to take up water from air. Orthorhombic. Density 2·75.
$CaSO_4,2H_2O$	*Gypsum.* Stable form in contact with water. Monosymmetric. Density 2·32.	*Soluble dihydrate.* First product of setting of plaster. Orthorhombic.

(*e*) *Solubility of Calcium Sulphate.*—The solubility of gypsum in water (Fig. 237) increases to a maximum of 0·21 per cent. at about 38°, and then diminishes. It is possible that 38° is a transition-temperature of ordinary monosymmetric gypsum into the orthorhombic form, the solubility of the first form increasing with rise of temperature, whilst that of the second form diminishes. Above 60° anhydrous calcium sulphate crystallises out, but its solubility in water decreases very rapidly, until at 220° it has fallen to 0·01 per cent. This fact is of importance in connection with the use of "permanently hard" water in boilers, since,

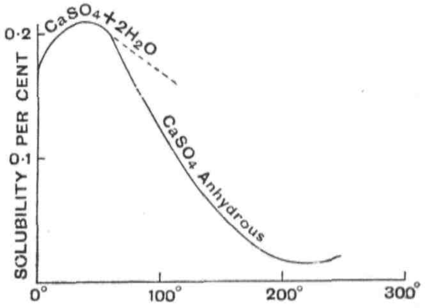


FIG. 237.—SOLUBILITY OF CALCIUM SULPHATE.

as the temperature of the water in the boiler rises, *e.g.*, to 150° or 180°, the calcium sulphate is deposited as a hard crystalline scale, which is very difficult to detach and causes much waste of heat, as well as other troubles; this "scaling" can be prevented either by very vigorous circulation of the water, or by "softening" it before use (p. 632).

Calcium sulphite, $CaSO_3$, is obtained as a white precipitate on mixing a solution of a calcium salt with sodium sulphite; it is almost insoluble in water, but dissolves in aqueous sulphurous acid, forming **calcium bisulphite,** $Ca(SO_3H)_2$, compare the bicarbonate, $Ca(CO_3H)_2$, a substance which is used very extensively in the manufacture of paper, and as a disinfectant in the brewing and sugar industries.

When a solution of calcium bisulphite is allowed to stand it loses sulphur dioxide, and crystals having the composition of a **dihydrate,**

$CaSO_3,2H_2O$, separate; this substance is probably a **calcium hydroxy-sulphite,** $HO\cdot Ca\cdot SO_3H,H_2O$, analogous to the magnesium hydroxy-carbonates (p. 618) which are formed in a similar manner:

$$Ca\begin{cases}SO_3H\\SO_3H\end{cases} + H_2O = Ca\begin{cases}OH\\SO_3H\end{cases},H_2O + SO_2.$$

Calcium sulphide, CaS, is obtained by heating calcium sulphate with powdered coke or coal,

$$CaSO_4 + 4C = CaS + 4CO,$$

or by passing hydrogen sulphide over incandescent lime. It was produced in very large quantities as a by-product in the manufacture of soda by the Leblanc process, and was worked up by allowing it to oxidise to calcium sulphite, thiosulphate, and polysulphides; when these are decomposed by acids, sulphur is deposited:

$$2CaS_2 + CaS_2O_3 + 6HCl = 3CaCl_2 + 3H_2O + 3S_2.$$

Sodium thiosulphate, $Na_2S_2O_3$, can also be prepared from the oxidised liquors by double decomposition:

$$CaS_2O_3 + Na_2CO_3 = CaCO_3 + Na_2S_2O_3.$$

Calcium sulphide, prepared by reduction from the sulphate, is only sparingly soluble in water and has the striking property of becoming phosphorescent after it has been kept in bright sunlight for a short time; this property is, however, dependent on the presence of traces of bismuth and alkali salts, and pure calcium sulphide does not show it.

Other Oxygen Salts.

Calcium Nitrate and Nitrite.

Calcium nitrate, $Ca(NO_3)_2$, is formed in the soil by the decomposition of nitrogenous organic matter under the influence of "nitrifying" bacteria, the activity of which is promoted by the presence of lime. It is manufactured on a large scale from dilute nitric acid (made by the Birkeland-Eyde method of extracting nitrogen from the air, p. 404) and limestone. It can also be made by double decomposition from sodium nitrate and calcium chloride,

$$2NaNO_3 + CaCl_2 = Ca(NO_3)_2 + 2NaCl;$$

the sodium chloride is separated out by concentrating the solution over a fire, and, after diluting a little to prevent any further separation of salt, the calcium nitrate is crystallised out in a hydrated form by cooling to atmospheric temperatures.

Anhydrous calcium nitrate forms a black translucent mass resembling pitch. It is very deliquescent and dissolves readily in water and in alcohol. The **tetrahydrate,** $Ca(NO_3)_2,4H_2O$, separates from solution in brilliant colourless crystals, which melt in their water of crystallisation

at 43°. These two forms of the nitrate are used for the preparation of ammonium nitrate,

$$Ca(NO_3)_2 + 2NH_3 + H_2O + CO_2 = CaCO_3 + 2NH_4NO_3.$$

The **basic nitrate,** $Ca(NO_3)_2,Ca(OH)_2$, crystallises with $2H_2O$ at 25°, or with $1H_2O$ at 100°, but loses this at 160°. The double salt is decomposed by water, but is less soluble and less deliquescent than the normal nitrate. The nitrate is therefore supplied in this form on a large scale for use as a fertiliser. Although calcium nitrate is less easy to handle, it is more effective for this purpose than ammonium sulphate, which renders the soil acid, or sodium nitrate, which is retained by the soil less readily than calcium nitrate.

Calcium nitrite, $Ca(NO_2)_2$, is formed, together with calcium nitrate, when oxides of nitrogen produced by the electrical process for extracting nitrogen from the air are absorbed by means of lime; it is less soluble than the nitrate and therefore separates in crystals from the liquor obtained by concentration.

Calcium Phosphates.

Phosphoric acid, H_3PO_4, gives three principal calcium salts, namely,

Tricalcium diphosphate, $Ca_3(PO_4)_2$;
Calcium hydrogen phosphate, $CaHPO_4$;
Monocalcium tetrahydrogen diphosphate, $CaH_4(PO_4)_2$.

Tricalcium diphosphate, $Ca_3(PO_4)_2$, occurs as PHOSPHORITE in large deposits in Florida (Florida ROCK PHOSPHATE), Tennessee, Algeria, and Tunis, as well as in certain islands of the Pacific (p. 419). It is a principal constituent of bones (55 to 65 per cent.), and the BONE ASH, prepared by igniting the bones of animals, consists mainly of this substance. It is insoluble in water, but dissolves to some extent in water containing carbon dioxide or organic acids, such as citric acid and acetic acid, probably owing to the formation of the soluble acid phosphate, $CaH_4(PO_4)_2$, which is prepared from it commercially by the action of sulphuric acid (see below). Finely ground rock phosphate is frequently used as a source of phosphoric acid in agriculture, when it is gradually dissolved and carried to the roots of the plants by carbonic acid and the organic acids of the soil; but as it only becomes available very slowly, the phosphate is usually converted into the soluble acid phosphate or "superphosphate" before use. The **fluorphosphate,** $Ca_5(PO_4)_3F$, which is an important mineral phosphate under the name of APATITE (Fig. 228, p. 624), and is also present in some slags, is much less soluble than the phosphates formulated above.

Calcium hydrogen phosphate, $CaHPO_4$, is insoluble in water, but soluble in a solution of ammonium nitrate. It is present in superphosphate manures, and, although much less soluble in water than the superphosphate, is considered to be of more value than the normal phosphates owing to its greater solubility in solutions of weak acids.

Monocalcium tetrahydrogen diphosphate, $CaH_4(PO_4)_2$, is the principal constituent of commercial SUPERPHOSPHATE. This is made by mixing finely powdered rock phosphate in a special mixer with just the requisite quantity of sulphuric acid. The mixture is dropped into large chambers, where the action represented by the equation

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O = CaH_4(PO_4)_2 + 2(CaSO_4,2H_2O)$$

is allowed to pass to completion, with the evolution of considerable heat, during the course of two to four days. The product is a massive cake consisting mainly of the acid phosphate and gypsum: it is removed with the help of a large drill and is sold as a powder.

BASIC SLAG (p. 769) is supposed to contain its phosphoric acid in the form of a **tetracalcium diphosphate,** $Ca_3(PO_4)_2,CaO$, which is insoluble in water but readily soluble in dilute nitric acid and even in solutions of ammonium nitrate. On account of its solubility in weak acids, the phosphoric acid of basic slag is assimilated by plants almost as easily as "superphosphate"; the excess of lime which it contains renders it particularly useful in soils which have become "acid" or "sour."

Calcium Silicates.

The most important natural silicate of lime is **calcium aluminomonosilicate,** $Ca(AlSiO_4)_2$, in the form of ANORTHITE or LIME-FELSPAR. **Calcium metasilicate,** $CaSiO_3$, is found as WOLLASTONITE, $CaSiO_3$; it changes into a dimorphous form known as PSEUDO-WOLLASTONITE when heated to 1200° and melts at 1540°. Wollastonite, which is a monosymmetric mineral of the "pyroxene" group (p. 509), combines with magnesium silicate to form **magnesium calcium silicate,** $MgCaSi_2O_6$, or DIOPSIDE (Fig. 227, p. 623); but it also forms solid solutions containing up to 17 per cent. of diopside.

Calcium orthosilicate, Ca_2SiO_4, undergoes changes of crystalline form at 675° and 1420° and melts at 2130°. A **sesquicalcium silicate,** $3CaO,2SiO_2$, which may perhaps be regarded as a double salt, $CaSiO_3$, Ca_2SiO_4, crystallises at about 1600° from a melt containing lime and silica in these proportions. A **tricalcium silicate** of the composition $3CaO,SiO_2$ has also been suggested as the active constituent of Portland cement; it has not been isolated in a pure state from mixtures of lime and silica, but crystallises out in a stable form from ternary mixtures of lime and silica with alumina.

Portland Cement.

When calcium carbonate, in the form of chalk, limestone, etc., is heated with clay, the lime attacks both the alumina and the silica, forming aluminates and silicates containing a high proportion of lime. This product when finely ground is known as PORTLAND CEMENT. When mixed with water, either alone, or with sand and stone to form CONCRETE, it sets in a few hours to a solid mass which grows steadily harder during a period extending over several years.

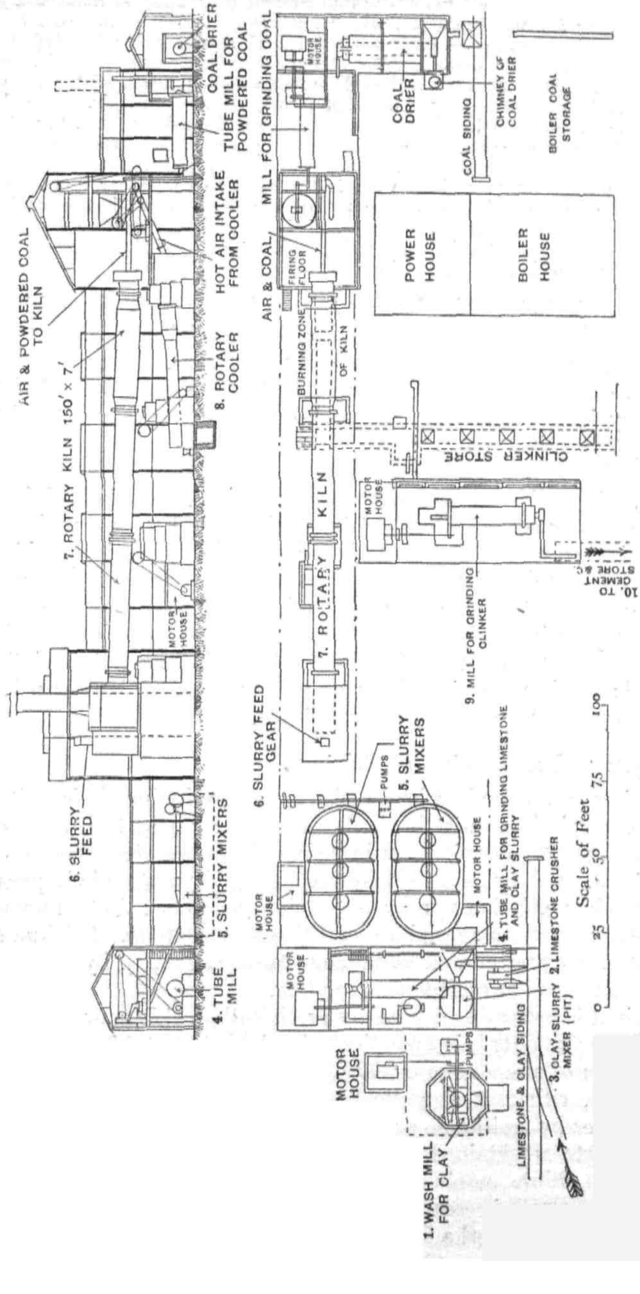


FIG. 238.—PLANT FOR MANUFACTURE OF PORTLAND CEMENT. (Edgar Allen & Co.)

Portland cement is commonly manufactured (Fig. 238) by making a thick cream of clay (1) and chalk (2), which are brought into a fine state of subdivision by passing the wet mixture (3) through a tube mill (4). This cream or SLURRY is mixed in large batches (5), and elevated to the top of a rotary kiln (7) from 100 to 250 feet in length, down which it flows, whilst the other end of the kiln is heated by a blast of powdered coal and air. The slurry emerges from the kiln in small nodules known as CEMENT CLINKER, which are cooled in a smaller revolving cylinder (8) by a current of air which is thus heated on its way to the kiln. The clinker is ground (9) until about 90 per cent. of it will pass through a sieve with 180 meshes to the linear inch, a small amount of gypsum being added to retard the setting. It is essential that the cement shall contain no free lime and it is necessary to regulate by analysis the ratio of lime to alumina and silica, this ratio varying according to the proportions in which the two oxides are present in the clay.

The setting of Portland cement depends on the decomposition by water of calcium aluminates and silicates containing too large a proportion of lime to be stable when water is present. The exact nature of these compounds is still uncertain, but it has been suggested that they may include a tricalcium aluminate, $3CaO,Al_2O_3$, and tricalcium silicate, $3CaO,SiO_2$.

Two theories have been put forward to explain the mechanism of the setting. According to the first, the new compounds formed by the action of water separate in a crystalline form, and the strength of the cement is due, as in the case of plaster of Paris, to the interlocking of minute crystals deposited from a supersaturated solution. The second theory suggests that the lime and other products of decomposition by water pass into solution and separate again in a gelatinous form, the strength of the cement being due to the drying up of this gelatinous material; further experimental work will be required, however, before this theory can be regarded as established.

Detection and Estimation of Calcium.

Calcium compounds when moistened with hydrochloric acid and heated on a platinum wire in the Bunsen flame impart to it an orange-red colour, but the principal line in the spectrum is a green line of wave-length 5589. Calcium salts are not precipitated by ammonia in presence of ammonium chloride nor by ammonium sulphide; but ammonium carbonate produces a precipitate of **calcium carbonate.** Calcium salts are completely precipitated as **calcium oxalate,** CaC_2O_4, by ammonium oxalate in neutral or ammoniacal solution.

Calcium is usually estimated by precipitation with ammonium oxalate, **calcium oxalate** being practically insoluble in water in presence of a slight excess of ammonium oxalate. The precipitate is washed, dried, and ignited, either at a gentle heat, which converts it into **calcium carbonate,** or by ignition in a muffle furnace or with the blowpipe, when **calcium oxide** is obtained. Small quantities of the oxalate may be dissolved in dilute sulphuric acid and titrated with potassium permanganate. Chalk is commonly estimated, *e.g.*, in a cement "slurry," by determining, with the help of a CALCIMETER, either the volume of

carbon dioxide set free, or the loss in weight which occurs, when the material is acted on by acids. Magnesium and calcium bicarbonates in a hard water can be estimated by direct titration against an acid, using methyl-orange as indicator; the soluble salts which give rise to permanent hardness can also be titrated by adding an excess of sodium carbonate, filtering off the insoluble carbonates, and titrating the excess of sodium carbonate against an acid (HEHNER'S METHOD). Hardness can also be measured directly by adding a standard solution of soap, until the water gives a permanent lather on shaking.

The atomic weight of calcium depends on exact determinations of the ratio $CaCO_3 : CaO$ in samples of calcite free from ferrous carbonate, $FeCO_3$, and of the ratio $CaCl_2 : 2Ag$.

38. STRONTIUM. Sr = 87·63.
56. BARIUM. Ba = 137·4.

Occurrence of Strontium and Barium.

Whereas magnesia and lime are amongst the principal constituents of igneous rocks, strontium and barium are present only in very small proportions (about 0·1 per cent. BaO and only traces of SrO). They are, however, found as sulphates and carbonates in mineral veins, where they have been segregated by deposition from aqueous solutions, *e.g.*,

Strontium sulphate	or CELESTINE,	$SrSO_4$.
Strontium carbonate	or STRONTIANITE,	$SrCO_3$.
Barium sulphate	or BARYTES,	$BaSO_4$.
Barium carbonate	or WITHERITE,	$BaCO_3$.

The carbonates are much less common than the sulphates and are perhaps derived from them by secondary changes. Important deposits of strontianite are found in Gloucestershire. Barytes is found in Derbyshire, Shropshire, and Devonshire, as well as in the north of England and the south-west of Ireland; it is also mined on a large scale in Germany, Spain, and the United States. The most important deposit of witherite in the world is at Settlingstones in Northumberland.

Strontium and its Compounds.

Strontium is the central member of a triad,

$$Ca = 40, \quad Sr = 88, \quad Ba = 137,$$

and is intermediate in its properties between calcium and barium.

Metallic strontium can be prepared like calcium by electrolysing the fused chloride. It is a white metal, of density 2·55, which tarnishes when exposed to moist air and melts at about 800°.

Strontium monoxide or **strontia,** SrO, is prepared by heating the carbonate or nitrate. It is manufactured commercially by heating celestine with carbon, which converts the sulphate into sulphide; this is decomposed by moist carbon dioxide and the carbonate is ignited

to convert it into the oxide. Strontia is a white powder which combines vigorously with water to form the hydroxide, $Sr(OH)_2$, liberating 19,000 calories,

$$SrO + H_2O = Sr(OH)_2 + 19{,}000 \text{ calories},$$

where lime gives 15,000 calories and baryta 23,000 calories. It unites with oxygen under a pressure of about 100 atmospheres at 400–500°, forming **strontium dioxide,** SrO_2, compare BaO_2.

Strontium hydroxide, $Sr(OH)_2$, is more soluble in water than lime, but less soluble than baryta ; thus, 100 grams of a saturated solution contain at 20°

0·123	gram	CaO,
0·69	,,	SrO,
3·36	grams	BaO.

Strontium hydroxide crystallises from solution as the **octahydrate,** $Sr(OH)_2,8H_2O$. It is used in extracting cane-sugar from molasses which will no longer deposit crystals ; on adding strontium hydroxide, strontium saccharate separates ; this is decomposed by carbon dioxide, setting free the sugar, which passes into solution, whilst strontium carbonate is precipitated.

Strontium carbonate, $SrCO_3$, in the form of STRONTIANITE is isomorphous with calcium carbonate in the form of aragonite, and is sometimes present as an impurity in the latter mineral. It can be prepared artificially by precipitating a soluble strontium salt with an alkaline carbonate.

Strontium sulphate, $SrSO_4$, is the principal raw material from which strontium compounds are prepared. The crystals of CELESTINE are isomorphous with barytes, $BaSO_4$, and with anglesite, $PbSO_4$, but not with anhydrite, $CaSO_4$, although this may be present as an isodimorphous impurity in celestine. Strontium sulphate is much less soluble in water than calcium sulphate, but more soluble than barium sulphate ; 100 grams of a saturated solution contain at 18°

0·20	gram	$CaSO_4$,
0·0114	,,	$SrSO_4$,
0·00023	,,	$BaSO_4$.

These differences in solubility are used to distinguish and to separate the three metals. Strontium sulphate is readily reduced to **strontium sulphide,** SrS, from which the chloride and nitrate are commonly prepared.

Strontium chloride, $SrCl_2$, is prepared by dissolving the sulphide or carbonate in hydrochloric acid. It dissolves readily in water, and crystallises out as the **hexahydrate,** $SrCl_2,6H_2O$; the crystals are deliquescent (compare calcium chloride).

Strontium nitrate, $Sr(NO_3)_2$, is prepared by dissolving the sulphide or carbonate in nitric acid. It is readily soluble in water, but, unlike calcium nitrate, is almost insoluble in alcohol. It is used in pyrotechny to produce a crimson flare.

Detection and Estimation of Strontium.

Strontium salts are easily recognised by the brilliant crimson coloration which they impart to a flame and by the red, green, and blue lines of the flame spectrum. **Strontium carbonate,** $SrCO_3$, is precipitated, with $CaCO_3$ and $BaCO_3$, by ammonium carbonate, even in presence of ammonium chloride, which retains magnesium carbonate in solution. **Strontium sulphate** is precipitated by a saturated solution of calcium sulphate, but only on boiling, a fact which distinguishes strontium salts from those of barium.

Strontium is usually estimated by precipitating it as strontium sulphate in presence of alcohol. It can be separated from calcium, by precipitating as carbonate, dissolving in nitric acid, evaporating, and extracting with absolute alcohol, which dissolves calcium nitrate and leaves strontium nitrate undissolved.

The atomic weight of strontium is based on determinations of the ratios $SrBr_2 : 2AgBr : 2Ag$; $SrCl_2 : 2AgCl : 2Ag$; $SrBr_2$ and $SrCl_2 : SrSO_4$.

Preparation and Properties of Metallic Barium.

Metallic barium, like metallic calcium, cannot be prepared by reducing the oxide or carbonate with carbon, since under these conditions **barium carbide,** BaC_2, is formed ; this resembles calcium carbide, but yields **barium cyanide,** BaC_2N_2 (instead of barium cyanamide, $BaCN_2$, and carbon), when heated in nitrogen.

Barium amalgam can be prepared by electrolysing a solution of barium chloride with a mercury cathode ; when distilled in a current of hydrogen it gives barium hydride, and on heating this in a vacuum to about 900° hydrogen is lost and metallic barium remains. Barium can also be prepared on a small scale by heating the oxide with aluminium at 1200°, when the metal distils out.

Barium is a silver-white metal of density 3·78, and is rather harder than lead. It melts above 850°, and can be distilled at slightly higher temperatures. It burns to the monoxide, BaO, and decomposes water, forming barium hydroxide, $Ba(OH)_2$. It also acts upon alcohol, forming **barium ethoxide,** $Ba(OC_2H_5)_2$ (compare sodium ethoxide, p. 150).

Barium Oxides, Hydroxide, and Carbonate.

Barium monoxide, or **baryta,** BaO, is formed from the carbonate only by heating to extremely high temperatures ; the carbon dioxide can, however, be eliminated without difficulty by reduction to carbon monoxide, *e.g.*, by heating the carbonate with charcoal,

$$BaCO_3 + C = BaO + 2CO.$$

It is now manufactured also from the sulphate by heating with coke in the electric furnace, when carbon monoxide and sulphur dioxide are evolved,

$$BaSO_4 + C = BaO + CO + SO_2.$$

A porous form of barium monoxide, suitable for conversion into the peroxide, is obtained by heating a mixture of barium carbonate and nitrate with heavy petroleum.

The oxide is a white mass, which readily absorbs water and carbon dioxide; it dissolves in boiling water, forming the hydroxide. When heated in the air at about 500° it absorbs oxygen, forming **barium peroxide,** BaO_2; when this is heated at 800°, or under reduced pressure, it loses oxygen again and forms the monoxide,

$$2BaO + O_2 \rightleftarrows 2BaO_2.$$

These changes were formerly used in the separation of oxygen from the air by BRIN'S PROCESS (p. 229).

Barium hydroxide, $Ba(OH)_2$, is obtained by dissolving the oxide in boiling water; flaky crystals of the **octahydrate,** $Ba(OH)_2,8H_2O$, separate on cooling (compare strontium hydroxide). It is prepared on a large scale by heating barium sulphate with carbon to form the sulphide, and passing moist carbon dioxide over the heated product to convert it into carbonate,

$$BaS + CO_2 + H_2O = BaCO_3 + H_2S;$$

superheated steam is then used to convert the carbonate into the hydroxide,

$$BaCO_3 + H_2O = Ba(OH)_2 + CO_2.$$

Barium hydroxide is remarkably stable and only loses its water at very high temperatures. It dissolves in water, forming a strongly alkaline solution containing nearly 4 per cent. (or more than half an equivalent per litre) of $Ba(OH)_2$ at 20°; this solution is known as BARYTA WATER, and is used in analysis when a caustic alkali free from carbonate is required.

Barium carbonate, $BaCO_3$, occurs naturally as WITHERITE in orthorhombic crystals, of density 4·3, isomorphous with aragonite and strontianite. It is far more stable towards heat than strontium or calcium carbonate, *e.g.*, the dissociation-pressure is only 2·7 mm. at 1000°, and becomes equal to 1 atmosphere only at 1350°; the conversion of the carbonate to oxide is, therefore, effected by heating it with coke, so as to reduce the carbon dioxide to carbon monoxide. Barium carbonate is almost insoluble in water (0·02 gr. per litre), but considerably more soluble in presence of carbon dioxide, probably owing to the formation of a bicarbonate. It is used on a large scale for preparing other compounds of barium, and also for purifying common salt (see p. 560). Its most extensive use is probably in separating organic sulphonic acids from the sulphuric acid used in preparing them; the barium salts of the sulphonic acids are usually soluble in water and can be filtered from the insoluble residue of barium sulphate and carbonate. Chalk is also used for this purpose, as it is very much cheaper, but it has the disadvantage that very considerable quantities of calcium

sulphate are often retained in solution, whereas barium sulphate is almost completely insoluble.

Barium Sulphate and Sulphide.

Barium sulphate, $BaSO_4$, occurs naturally as BARYTES or HEAVY SPAR, in massive veins, associated frequently with galena or blende, and is mined in very large quantities, the annual output being more than 300,000 tons. It forms transparent orthorhombic crystals (Fig. 239) of density 4·5, which cleave readily into rhombic prisms (Fig. 4, p. 5) and are isomorphous with strontium sulphate, but not with anhydrite. The finely ground mineral is used as a basis for paints instead of white lead, for weighting rubber and paper, and for many other purposes

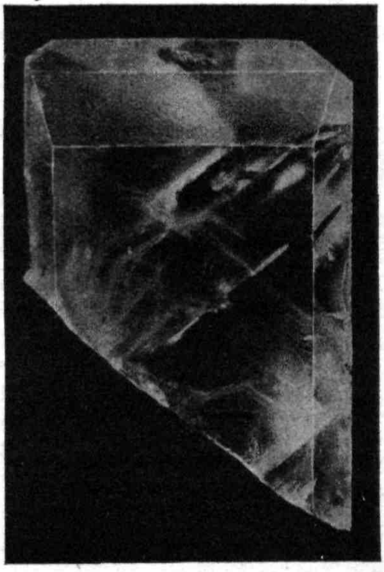


FIG. 239.—ORTHORHOMBIC CRYSTAL OF BARYTES. (British Museum, Natural History.) Notice the cracks indicating the cleavage into rhombic prisms as shown in Fig. 4, p. 5.

Barium sulphate is practically insoluble in water (2·3 mg. per litre or one part in 430,000 at 18°) and also in dilute acids ; it is therefore used in analysis in estimating sulphuric acid and sulphates. Precipitated barium sulphate is also manufactured on a large scale by heating barytes with coke, so as to form a mixture of barium sulphide and oxide, dissolving the product in water, and precipitating the solution with sodium sulphate ; it is used under the name of BLANC FIXE or PERMANENT WHITE as a pigment, which is not poisonous and does not blacken on exposure to air. A mixture of barium sulphate and zinc sulphide is also manufactured as a pigment under the name of LITHOPONE ; the mixture is precipitated from barium sulphide and zinc sulphate,

$$BaS + ZnSO_4 = BaSO_4 + ZnS ;$$

when the mixed precipitate is heated, the two compounds become associated together in a peculiar way and give rise to a valuable white paint.

Barium sulphide, BaS, is prepared by reducing barium sulphate with coke or coal. Like crude calcium sulphide, the anhydrous compound is phosphorescent. It dissolves readily in water, forming the hydroxide and hydrosulphide,

$$2BaS + 2H_2O = Ba(SH)_2 + Ba(OH)_2,$$

but under special conditions can be crystallised out as an unstable **hexahydrate,** $BaS,6H_2O$.

In addition to its use in making lithopone, and in the preparation of barium salts from barytes, barium sulphide is used to precipitate lead from tartaric acid, and arsenic from sulphuric acid ; hydrogen sulphide is liberated, which precipitates the impurity, whilst the whole of the barium is precipitated as tartrate or sulphate.

Soluble Salts of Barium.

Barium chloride, $BaCl_2$, is prepared by dissolving either witherite or barium sulphide in dilute hydrochloric acid,

$$BaCO_3 + 2HCl = BaCl_2 + H_2O + CO_2.$$

It is also prepared by heating barytes with calcium chloride and coal at 900°,

$$BaSO_4 + 4C + CaCl_2 = BaCl_2 + CaS + 4CO ;$$

the barium chloride is extracted with hot water and crystallised out from the solution. Barium chloride is soluble in water and separates from it as the **dihydrate,** $BaCl_2,2H_2O$. Unlike calcium chloride, it is not deliquescent. It is used in analysis for the detection of soluble sulphates, which convert it into barium sulphate.

Barium nitrate, $Ba(NO_3)_2$, is prepared by dissolving witherite in hot nitric acid, and evaporating the solution to the crystallising point. It can also be prepared by the action of dilute nitric acid on barium sulphide, or by mixing hot solutions of barium chloride and sodium nitrate, when barium nitrate separates in crystals on cooling. It is sparingly soluble in water ; a saturated solution contains 8 per cent. of barium nitrate at 20° as compared with 26 per cent. of barium chloride. It is used in pyrotechny to produce a green fire, and in the preparation of certain explosives.

Detection and Estimation of Barium.

The Bunsen flame is coloured green by a trace of a barium compound, moistened with hydrochloric acid ; the spectroscope shows a complex spectrum with characteristic lines in the green.

Soluble barium salts are not precipitated by hydrogen sulphide, by ammonia, or by ammonium sulphide, but are thrown down by ammonium carbonate as **barium carbonate**, and thus show the same behaviour as calcium and strontium salts ; they are distinguished from these by giving an immediate precipitate of **barium sulphate** in the cold with a solution of calcium sulphate. On adding acetic acid and potassium chromate to a solution containing barium, strontium, and calcium salts, **barium chromate** is precipitated as a lemon-yellow pigment, whilst calcium and strontium remain in solution.

Barium is estimated quantitatively in the form of the insoluble

sulphate, which is also the compound commonly selected for the gravimetric estimation of sulphur.

The atomic weight of barium is based on determinations of the ratios $BaCl_2 : 2AgCl : 2Ag$ and $BaBr_2 : 2Ag$.

4. Beryllium or Glucinum. Be or Gl = 9·1.

Occurrence.

Beryllium occurs as a **beryllium aluminium metasilicate,** $Be_3Al_2(SiO_3)_6$ (compare garnet, $Ca_3Al_2(SiO_4)_3$, which is an orthosilicate), in the mineral BERYL. Pure beryl is colourless but is not often found; the transparent green forms of beryl are known as EMERALD and the bluish-green forms as AQUAMARINE; blue, yellow, grey, and rose-coloured varieties of beryl also occur, the colour in all cases being due to traces of impurities such as chromium (emerald) or manganese. CHRYSOBERYL is a **beryllium aluminate,** $BeAl_2O_4$; it is totally distinct in crystalline form from the spinels, such as $MgAl_2O_4$ and $ZnAl_2O_4$, but is isomorphous with OLIVINE, Mg_2SiO_4; this contains the same number of atoms in the molecule as Al_2BeO_4, although the valencies are distributed quite differently (compare $CaCO_3$ and $NaNO_3$, p. 631).

Preparation and Properties of Beryllium.

(*a*) *Classification.*—Beryllium resembles aluminium so closely that its inclusion with magnesium amongst the elements of the alkaline earths is justified almost exclusively by its valency and by the formulæ of its compounds; it was indeed only after its valency had been altered from 3 to 2, and its atomic weight from 14 to 9, with a corresponding revision of the formulæ of all its compounds, that it was separated from the element aluminium to which it was obviously related most closely. This tendency for the first member of a family of elements to resemble those of the succeeding family has already been noted in the case of boron and silicon (p. 482), oxygen and chlorine, and amongst the metals in the case of lithium (p. 609).

(*b*) *Preparation.*—Beryllium can be separated by heating beryl with sodium silicifluoride and extracting the element as sodium beryllium fluoride, $NaBeF_3$ or Na_2BeF_4, a salt which differs from cryolite, Na_3AlF_6, in being soluble in water. Metallic beryllium was prepared by heating beryllium chloride, $BeCl_2$, with potassium (Wöhler, 1828), or by heating potassium beryllium fluoride, K_2BeF_4, with metallic sodium in a steel crucible:

$$BeCl_2 + 2K = Be + 2KCl,$$
$$K_2BeF_4 + 2Na = 2KF + 2NaF + Be.$$

It can also be prepared by electrolysing the fused double fluoride, $NaBeF_3$ or Na_2BeF_4.

(*c*) *Properties.*—Beryllium is a white ductile metal, of density 1·9,

and melts at 1280°. It does not alter in the air, and, unlike magnesium, does not decompose water even at 1000°. Like aluminium, it is soluble both in dilute acids and in alkalies, but does not dissolve in nitric acid, either dilute or concentrated. It has recently been used in small proportions in certain alloys.

Compounds of Beryllium.

Beryllium oxide or **beryllia,** BeO, is obtained as an insoluble earth (compare alumina) by igniting the carbonate, the hydroxide, or the sulphate (compare aluminium sulphate).

Beryllium hydroxide, $Be(OH)_2$, is precipitated as a gelatinous mass when ammonia is added to a solution of a soluble salt of the metal, but dissolves readily in an excess of sodium or potassium hydroxide (compare aluminium hydroxide).

Beryllium carbonate, $BeCO_3,4H_2O$, is abnormal in its properties, being soluble in water and unstable; it readily loses carbon dioxide and is probably a hydroxycarbonate, $HO{\cdot}Be{\cdot}CO_3H,3H_2O$ (compare magnesium hydroxycarbonate, $HO{\cdot}Mg{\cdot}CO_3H,2H_2O$).

Beryllium chloride, $BeCl_2$, is obtained in the anhydrous condition

(i) By heating the metal in a current of chlorine or of hydrogen chloride.

(ii) By heating the oxide with carbon in a current of chlorine (compare aluminium chloride),

$$BeO + Cl_2 + C = BeCl_2 + CO.$$

(iii) By heating the oxide in the vapour of carbon tetrachloride,

$$2BeO + CCl_4 = 2BeCl_2 + CO_2.$$

It is a fusible white powder which is easily sublimed (compare aluminium chloride). Like aluminium chloride, it fumes in moist air, liberating hydrogen chloride,

$$BeCl_2 + H_2O = 2HCl + BeO.$$

It dissolves readily in water, with liberation of heat, and separates again as the **tetrahydrate,** $BeCl_2,4H_2O$, in deliquescent plates like magnesium chloride.

Beryllium sulphate, $BeSO_4$, is soluble in water and separates as a tetrahydrate, $BeSO_4,4H_2O$; a hexahydrate, dihydrate, and monohydrate are also known (compare magnesium sulphate).

Beryllium nitrate, $Be(NO_3)_2,3H_2O$, is crystallised with difficulty and is very deliquescent; it is easily soluble in alcohol.

CHAPTER XXXIV

ALUMINIUM AND THE EARTHS

Atomic Number.	*Element.*	*Symbol.*		*Atomic Weight.*
5	Boron	B	=	11·0
13	Aluminium	Al	=	27·1
21	Scandium	Sc	=	45·1
39	Yttrium	Yt	=	88.7
57—71	Metals of the rare earths.	La to Lu	=	139·0 to 174·0

Classification.

The metals of the alkaline earths are followed in the periodic classification of the elements by the metals of the earths, of which alumina, Al_2O_3, is the type. These are weaker bases than the alkalies or the alkaline earths, and alumina itself is an amphoteric oxide (p. 529) which exhibits both basic and acid properties. Boron, which appears at the head of the family in the preceding table, is an element of totally different type, resembling silicon instead of aluminium, and has already been described as a non-metal in Part II (p. 515). The real analogue of aluminium is found, in the preceding column of the periodic table, in beryllium, the characteristic metal of the earth beryllia. This element was removed from the aluminium into the magnesium group as the result of a determination of the vapour-density of the chloride, which showed it to be bivalent instead of tervalent; the formulæ of its compounds, therefore, resemble those of the compounds of magnesium, although its properties resemble those of aluminium more closely than those of any other element. The remainder of the group includes the elements of 16 " rare earths " which are found in nature as complex mixtures of isomorphous phosphates, and resemble one another so closely that their separation has proved to be a matter of extraordinary difficulty. They have, however, acquired considerable commercial importance as a result of the use of ceria with thoria in incandescent gas mantles, and are now available in large quantities as by-products of this industry.

Physical Properties.

The physical properties of these elements are shown in the following table :—

TABLE 72.—PHYSICAL PROPERTIES OF THE ALUMINIUM GROUP.

	Density.	*Melting-point.*	*Boiling-point.*
B . .	2·5	Vaporises in the electric arc.	
Al . .	2·70	659°	1800°
Sc . .	—	—	—
Yt . .	3·8	—	—
La . .	6·1	810°	—

Aluminium is a light metal with a silvery-white lustre which it retains to a large extent on exposure to air. It melts at a dull red heat, but oxidises and burns if heated rather more strongly.

Valency and Isomorphism.

An important feature of this group of elements is the tervalency which appears in all their compounds and which is quite as fixed a characteristic of the earths as the bivalency of the alkaline earths or the univalency of the alkalies. Thus, the typical compounds of aluminium are represented by formulæ such as $AlCl_3$ (or Al_2Cl_6), Al_2O_3, $Al(NO_3)_3$, $Al_2(SO_4)_3$, and $AlPO_4$, and the quadrivalent compounds of cerium, such as CeO_2, $Ce(NO_3)_4$, and $Ce(SO_4)_2$, are the only important exceptions to the general rule.

Three important groups of compounds of aluminium are the **spinels**, such as $MgAl_2O_4$, the **alums,** such as $KAl(SO_4)_2,12H_2O$, and the **felspars,** such as $KAlSi_3O_8$. Each of these compounds is the starting-point of an isomorphous series in which the *aluminium* may be replaced by other tervalent elements, such as ferric iron or chromium, whilst *potassium* may be replaced by sodium or other univalent radicals, and *magnesium* by zinc, calcium, or ferrous iron.

13. ALUMINIUM. Al = 27·1.

Occurrence.

(*a*) *Aluminium Silicates.*—After silicon and oxygen, aluminium is the most abundant element in the solid crust of the earth, which contains 15 per cent. of alumina, Al_2O_3, or nearly 8 per cent. of aluminium as contrasted with 4·5 per cent. of iron.

(i) The alumina in igneous rocks is usually combined with silica to form ALUMINO-SILICATES (p. 502), as in the FELSPARS (Figs. 193 and 194, pp. 502 and 503, compare also Fig. 183, p. 484, and Fig. 242, p. 663):

Potassium alumino-trisilicate, or POTASH FELSPAR, $KAlSi_3O_8$;
Sodium alumino-trisilicate, or SODA FELSPAR, $NaAlSi_3O_8$;
Calcium alumino-monosilicate, or LIME FELSPAR, $Ca(AlSiO_4)_2$.

In all these compounds a part of the aluminium may be replaced by ferric iron.

(ii) Alumina is also associated with silica as a constituent of the MICAS (p. 504), *e.g.*,

MUSCOVITE, $KH_2(AlSiO_4)_3$ (Fig. 196, p. 505);
PHLOGOPITE, $KH_2Mg_3Al(SiO_4)_3$ (Fig. 197 (p. 506);
BIOTITE, $KHMg_2Al_2(SiO_4)_3$;
LEPIDOLITE, $Li_3(AlF_2)Si_3O_8$.

Thus MUSCOVITE is a **potassium hydrogen alumino-silicate** formed by eliminating two-thirds of the alkali and two-thirds of the silica from felspar, *e.g.*, *by the action of water under pressure. When the whole of* the potash is eliminated, as in the weathering of felspar by exposure to

FIG. 240.—CRYOLITE (natural size). (British Museum, Natural History.) Notice the pseudo-cubic form and cleavage of the crystals.

water and carbon dioxide, the felspar is converted into CHINA CLAY, the principal constituent of which is KAOLINITE, $H_4Al_2Si_2O_9$—compare serpentine, $H_4Mg_3Si_2O_9$. Common clay is formed in a similar manner, but is coloured blue, green, or brown, by compounds of iron derived from the original igneous rock.

(iii) A simple **aluminium monosilicate,** Al_2O_3,SiO_2, or Al_2SiO_5, is found as SILLIMANITE (p. 662), and kaolinite may be regarded as a hydrated **aluminium disilicate,** $Al_2O_3,2SiO_2,2H_2O$ or $Al_2Si_2O_7,2H_2O$.

(*b*) *Aluminium Oxide.*—When the silica as well as the alkali is removed from felspar, alumina is left behind as a **hydrated oxide,** Al_2O_3, aq., compare limonite, Fe_2O_3, aq. Vast deposits of these two oxides are found in India as LATERITE, whilst deposits which are free from iron are found in the South of France and elsewhere as BAUXITE, and form the principal ore of aluminium. Anhydrous **aluminium oxide,**

Al_2O_3, is found as CORUNDUM or EMERY; crystals coloured red by chromium are known as RUBY, and blue crystals are known as SAPPHIRE.

(*c*) *Fluoride.*—Large deposits of **sodium alumino-fluoride,** Na_3AlF_6, or CRYOLITE (Fig. 240), are found in Iceland, and used with bauxite in the manufacture of aluminium. TOPAZ, $(AlF_2)AlSiO_4$ (Fig. 242, p. 663), and LEPIDOLITE, $(AlF_2)Li_3Si_3O_8$, may also be regarded as derivatives of aluminium fluoride.

Preparation of Metallic Aluminium.

(*a*) *By Reduction.* Aluminium was first prepared in 1827 by Wöhler, who reduced the chloride by means of metallic potassium. It was first manufactured commercially in 1855 by the action of sodium on the

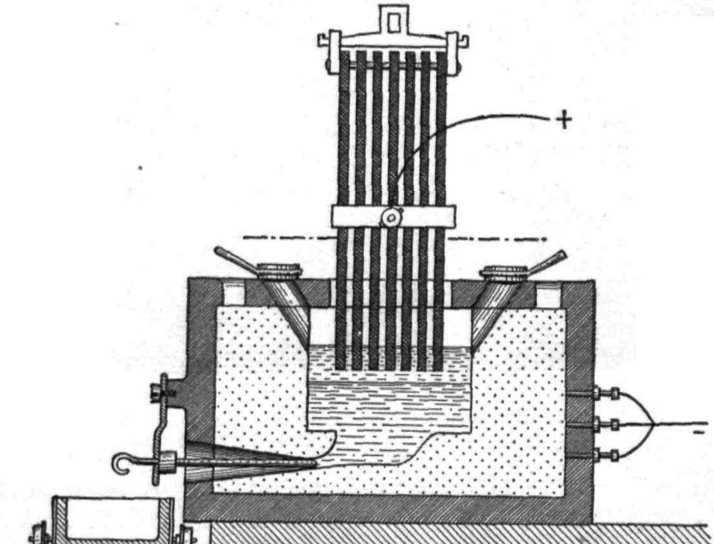


FIG. 241.—MANUFACTURE OF ALUMINIUM.

double chloride, $NaCl,AlCl_3$ or $NaAlCl_4$, prepared by heating precipitated alumina with salt and coal-dust in a current of chlorine:

$$3Cl_2 + Al_2O_3 + 3C = 2AlCl_3 + 3CO,$$
$$AlCl_3 + 3Na = 3NaCl + Al.$$

(*b*) *By Electrolysis.* Aluminium is now prepared by the electrolysis of a fused mixture of cryolite and purified bauxite. The simplest interpretation of this action is to assume that the cryolite acts merely

as a solvent for the bauxite, which is decomposed by the current according to the equation

$$2Al_2O_3 = 4Al + 3O_2.$$

It is, however, possible that the sodium salt is first decomposed by the current according to the equation

$$Na_3AlF_6 = 3Na + \mathit{AlF_6},$$

aluminium being set free by the secondary action of the sodium upon the cryolite, whilst the $\mathit{AlF_6}$ radical attacks the bauxite and converts it into fluoride with liberation of oxygen as shown in the equations

$$3Na + Na_3AlF_6 = Al + 6NaF,$$
$$4\mathit{AlF_6} + 2Al_2O_3 = 8AlF_3 + 3O_2.$$

The apparatus used in the manufacture of aluminium is shown in Fig. 241. It consists of an iron box lined with carbon, which serves as the cathode, and a series of carbon anodes. Cryolite is melted in the box by the electric current. and alumina is then added. Aluminium is liberated by the electric current and sinks to the bottom of the bath, whilst the carbon anodes are burnt to oxides. The normal voltage between the electrodes is 5 to 6 volts. The electrical resistance generates sufficient heat to keep the cryolite liquid, but increases as the alumina is used up, until, at the end of about two hours, more alumina is added to replace that which has been decomposed by the current. The alumina is freed from iron by a wet process (p. 660) or by a preliminary heating in an electric furnace with enough carbon to reduce and melt out the iron.

Physical Properties of Aluminium.

Aluminium is a silver-white metal which retains a dull lustre even on prolonged exposure to the air. It is a light metal of density 2·7. It melts at 659° and can be cast by heating it to a temperature at which a dull red glow can just be seen in a darkened room. The metal can be rolled into foil, stamped, and drawn into wire. Its electric conductivity is 60 per cent. of that of an equal volume of copper, or 200 per cent. for a conductor of equal weight ; thus, although copper is almost always used for electric cables which have to be coated with an insulator, aluminium has frequently been used where naked conductors can be employed, and this type of construction provides a useful alternative in case the price of copper cables should increase unduly

Alloys of Aluminium.

Aluminium is the basis of an important series of LIGHT ALLOYS The pure metal is rather soft, and when cast has a tensile strength of only 5 tons per square inch, as compared with about 9 tons for cast copper and about 22 tons for wrought iron ; but on account of its low

density it could support a column of its own material about 1·8 miles in length, as compared with about 1 mile for copper, and about 3 times this length for wrought iron. The tensile strength of the cast metal can be raised from 5 or 6 to about 12 tons per square inch by rolling into sheet.

Aluminium forms alloys rather less readily than the majority of the metals. Thus even in the liquid state it sinks as a separate layer under sodium and potassium, and floats on lead, bismuth, and cadmium, the approximate composition of the two layers being as follows :—

	Upper Layer.				*Lower Layer.*			
At 800°	Al	98·09	Pb	1·91	Pb	99·93	Al	0·07
At 800°	Al	97·98	Bi	2·02	Bi	99·72	Al	0·28
At 750°	Al	96·61	Cd	3·39	Cd	99·78	Al	0·22

Its power of forming solid solutions is also very limited, except in the case of zinc, of which it can take up 40 per cent.

Solid solutions of aluminium and copper can be formed containing up to 9 per cent. of aluminium at one end of the series, and up to 4 per cent. of copper at the other end. The former series of alloys are used as ALUMINIUM BRONZES ; they have a tensile strength up to 38 tons per square inch, and possess the valuable quality of being very resistant to corrosion by sea-water. An alloy of the latter series, containing 4 per cent. of copper, has a tensile strength of 10 tons per square inch as compared with 5 tons for aluminium, and this can be increased to 20 tons by rolling or drawing. A similar alloy containing 4 per cent. of copper with about ½ per cent. each of manganese and of magnesium is known as DURALUMIN, and is one of the most important of the light alloys ; its density is similar to that of aluminium, but it possesses the remarkable property that, when heated for half an hour at about 500° and then quenched in water, its tensile strength increases in the course of 4 or 5 days from 18 to 26 tons per square inch ; in the latter condition it would support a column of its own material up to 9 miles in length.

Alloys of aluminium containing up to 30 per cent. of zinc (usually 13 per cent. of zinc with 3 per cent. of copper and up to 1 per cent. of iron) are of considerable technical importance, since they give very sound castings ; they are used for motor-car crank cases. Aluminium (about 2 per cent.) is also added to brass in order to harden it ; its tensile strength may be increased in this way to a value comparable with that for mild steel, *e.g.*, 30 tons per square inch, without any marked loss of ductility. Aluminium containing from 2 to 10 per cent. of magnesium is known as MAGNALIUM ; it is lighter than aluminium and is similar to brass in its mechanical properties.

Chemical Properties of Aluminium.

(*a*) *Oxidation*.—Aluminium has a very great affinity for oxygen, as may be seen by a comparison of the heats of formation of the following oxides :—

MgO	143,000
$\frac{1}{3}Al_2O_3$	127,000
Na_2O	100,000
ZnO	85,000
H_2O	68,360
$\frac{1}{3}Fe_2O_3$	65,000
$\frac{1}{2}CO_2$	48,000
CO	29,000

These heats of formation explain the fact that aluminium cannot be prepared from its oxide by reduction with hydrogen, with carbonic oxide, or with carbon: incidentally they confirm the view that the preparation of sodium and of zinc by reduction with carbon depends on the volatility of these metals and not on a weak affinity for oxygen.

In view of its position in this table, it is remarkable that aluminium is not easily ignited and does not readily tarnish in air; moreover, it does not dissolve in nitric acid, although it is readily soluble in dilute hydrochloric or sulphuric acid. These facts are explained most readily by assuming that aluminium becomes covered with a thin film of oxide which is not permeable to air or water, and therefore acts like a protective varnish. This view finds support in the dull lustre of the metal, which is in marked contrast with the bright lustre of silver, and also in its behaviour when amalgamated with mercury; the mercury appears to break up the surface film, with the result that a feathery growth of oxide can be seen springing up rapidly from the surface of the metal, which becomes quite warm with the heat of oxidation. Again, when aluminium is made the anode of an electrolytic cell, the oxidised surface immediately acquires a resistance that stops the passage of the electric current; but the conductivity is restored at once when the aluminium again becomes the cathode. This property is made use of in the construction of ELECTROLYTIC RECTIFIERS, in which an alternating current is turned into a direct current by allowing it to flow only in one direction. The behaviour of these rectifiers is in harmony with the view that when aluminium becomes oxidised, the oxide forms a continuous and impermeable insulating film or varnish on the surface of the metal. It is of interest to notice that somewhat similar qualities can be developed in metallic chromium and in metallic iron by dipping them in concentrated nitric acid, when the metals become "passive." Further evidence of the intensity of the affinity between aluminium and oxygen is found in the use of aluminium as a reducing agent in the GOLDSCHMIDT PROCESS for the preparation of metals such as chromium,

which cannot be reduced from their ores by means of carbon, and in the use of a mixture of aluminium with oxide of iron to set free metallic iron at a very high temperature. This mixture, known as THERMITE, has been used in incendiary bombs, and industrially for welding iron and steel, *e.g.*, tram-rails are welded together by casting round the joint metallic iron at so high a temperature that the ends of the rails are partially fused and become firmly united together:

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe.$$

The mixture is not easily ignited, but may be fired by means of a fuse of magnesium ribbon dipping into a small quantity of an ignition mixture of aluminium powder and barium peroxide; the combustion of the thermite is then so rapid that it is possible to pour the molten iron from a crucible before its walls have become hot.

(*b*) *Combination with other non-metals.*—Aluminium combines directly not only with oxygen, but also with chlorine and sulphur, and with nitrogen, to form a **nitride,** AlN, which is decomposed by water with liberation of ammonia. When attempts are made to prepare aluminium by reducing the oxide with carbon in the electric furnace, the metal (like calcium) unites with carbon to form a **carbide,** Al_4C_3, which is of interest because it yields marsh gas and not acetylene when decomposed by water:

$$Al_4C_3 + 6H_2O = 2Al_2O_3 + 3CH_4.$$

Aluminium does not combine directly with hydrogen, but compounds such as **aluminium trimethyl,** $Al(CH_3)_3$, are known, which may be regarded as analogous to the unknown hydride, AlH_3.

Uses of Aluminium.

Aluminium is used in the construction of vessels for cooking and for many chemical operations in which an inert container is required; it is of particular value in the preparation of foodstuffs, where the harmless character of its compounds gives it a substantial advantage over copper and tin, and in the preparation of products which would be spoilt by the colouring effect of a trace of iron. Its resistance to nitric acid is of particular importance in chemical plant. It is used as a reducing agent in explosives, where it is mixed with compounds such as ammonium nitrate and ammonium perchlorate which contain an excess of oxygen. It is used in a finely divided state as a metallic paint and is the basis of some important alloys (p. 656)

The compounds of aluminium are used extensively as pure products, such as alum, in dyeing and in the preparation of paints; and in an unpurified form as emery, clay, felspar and mica; bricks, porcelain, and cement, as well as the hard igneous rocks used as road-metal and for building, consist very largely of aluminium silicates with oxides of other metals.

COMPOUNDS OF ALUMINIUM.

Aluminium Fluoride, AlF_3.

Aluminium fluoride, like calcium fluoride, is insoluble in water. In the form of CRYOLITE, $3NaF,AlF_3$, a colourless mineral of low melting-point (Fig. 240), it is important as one of the materials used in the preparation of aluminium. Cryolite has also been used as a source of sodium carbonate; when heated with chalk it gives a mixture of calcium fluoride with sodium aluminate, from which, by the action of carbon dioxide, sodium carbonate and pure alumina are obtained:

$$Na_3AlF_6 + 3CaCO_3 = Na_3AlO_3 + 3CaF_2 + 3CO_2,$$
$$2Na_3AlO_3 + 3CO_2 = 3Na_2CO_3 + Al_2O_3\ aq.$$

Aluminium is also associated with fluorine in TOPAZ, $(AlF_2)AlSiO_4$ (Fig. 242, p. 663), and in MICA (lepidolite).

Aluminium Chloride.

Anhydrous aluminium chloride can be prepared by the action of chlorine on aluminium. When used as a source of aluminium, it was prepared as a sublimate by the action of chlorine on a mixture of the precipitated oxide with charcoal,

$$3Cl_2 + Al_2O_3 + 3C = 2AlCl_3 + 3CO.$$

By adding common salt to the mixture a **double salt,** $NaCl,AlCl_3$, or $NaAlCl_4$, compare $NaBeF_3$ and $NaAuCl_4$, was obtained, which is less deliquescent than the chloride itself and was generally preferred for use in the manufacture of the metal.

A solution of the chloride is obtained by dissolving aluminium or its hydroxide in hydrochloric acid. Crystals of the **hexahydrate,** $AlCl_3,6H_2O$, separate from the solution, but these decompose when heated, losing hydrogen chloride and leaving a residue of alumina.

The anhydrous chloride melts at 190°, but vaporises at 183° under one atmosphere pressure, so that it usually sublimes without melting. It is very hygroscopic and fumes strongly in the air. It was formerly used as a source of aluminium, but is now employed chiefly in organic chemistry, where it is used as a catalyst to promote the separation of hydrogen chloride.

Aluminium Oxide or Alumina, Al_2O_3.

The crystalline mineral forms of alumina are very hard and very resistant to attack by acids or other chemical agents. The coloured varieties, containing traces of other oxides, are valued as gem-stones under the name of SAPPHIRE (blue) and RUBY (red), whilst the darker forms are used as abrasives under the name of CORUNDUM or EMERY.

Aluminium Hydroxide, $Al(OH)_3$.

Hydrated varieties of alumina occur naturally as DIASPORE, Al_2O_3,H_2O or $AlO(OH)$, and as BAUXITE, to which the formula

$Al_2O_3,2H_2O$, is commonly assigned. These are much more active than the anhydrous oxide and can be dissolved either in acids or in alkalies.

The **hydroxide,** $Al(OH)_3$ or $Al_2O_3,3H_2O$, can be precipitated in a gelatinous form by the action of ammonia on a soluble salt of aluminium, *e.g.*,

$$2AlCl_3 + 6NH_3 + 6H_2O = 2Al(OH)_3 + 6NH_4Cl,$$

but it dissolves again in an excess of caustic alkali.

Aluminium hydroxide is one of the weakest of the metallic bases. Although it is not precipitated from its salts by the addition of water, it is thrown down by ammonia even in presence of ammonium chloride,

$$AlCl_3 + 3NH_4{\cdot}OH = Al(OH)_3 + 3NH_4Cl\,;$$

this action is made use of in qualitative analysis to separate the tervalent hydroxides, $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$, from the stronger bivalent hydroxides

$$Zn(OH)_2,\ Mn(OH)_2,\ Co(OH)_2,\ Ni(OH)_2,$$
$$Mg(OH)_2,\ Ca(OH)_2,\ Sr(OH)_2,\ Ba(OH)_2,$$

which are not precipitated by this reagent, but on the contrary liberate ammonia from ammonium salts, *e.g.*,

$$Zn(OH)_2 + 2NH_4Cl = ZnCl_2 + 2NH_3 + 2H_2O.$$

The feeble basicity of aluminium hydroxide is further shown by the fact that it does not form a carbonate, so that carbon dioxide is set free when a carbonate is added to a soluble salt of aluminium, such as alum :

$$2KAl(SO_4)_2 + 3K_2CO_3 + 3H_2O = 4K_2SO_4 + 2Al(OH)_3 + 3CO_2.$$

In the same way, although aluminium will form a **sulphide,** Al_2S_3, by direct combination of the two elements, this is decomposed by the action of water with liberation of sulphuretted hydrogen,

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S.$$

Aluminates.

Like zinc hydroxide (p. 873), aluminium hydroxide is amphoteric and dissolves both in acids and in alkalies ; the alkaline solutions contain ALUMINATES in which alumina acts as the acid oxide. These aluminates are produced by the action of soda on bauxite,

$$Al_2O_3\,aq. + 2NaOH = 2NaAlO_2\,aq. + H_2O,$$

and of lime on cryolite (p. 659), as well as by heating together a mixture of chalk and clay in the manufacture of cement (p. 640). Some of them are too unstable to be crystallised from water, but an important series of mineral aluminates is known under the name of spinels, *e.g.*, SPINEL, $MgAl_2O_4$, and GAHNITE, $ZnAl_2O_4$; these are usually isomorphous mixtures, *e.g.*, [Mg,Ca,Fe] $[Al,Fe]_2O_4$, to which no simple formula can be assigned.

The solubility of aluminium hydroxide in alkalies is made use of in the purification of bauxite. The mineral is dissolved in caustic soda,

leaving behind the oxide of iron and other impurities. The alumina can be reprecipitated by carbon dioxide, but may also be separated merely by allowing the concentrated solutions to stand in contact with alumina, when the soda is recovered in a caustic form ready for further use.

Aluminium Sulphate and the Alums.

(*a*) **Aluminium sulphate,** $Al_2(SO_4)_3$, is an extremely soluble salt which crystallises from water with $18H_2O$, from aqueous alcohol with $9H_2O$, and from strong sulphuric acid with $6H_2O$. It can be prepared by the action of sulphuric acid on china clay,

$$Al_2Si_2O_7,2H_2O + 3H_2SO_4 = Al_2(SO_4)_3 + 2SiO_2 + 5H_2O,$$

the clear liquor being evaporated until it becomes solid on cooling. Aluminium sulphate can be dehydrated by evaporating to dryness, but at a red heat it decomposes completely into alumina, sulphur dioxide, and oxygen,

$$2Al_2(SO_4)_3 = 2Al_2O_3 + 6SO_2 + 3O_2.$$

It was by the analysis of this gaseous mixture of sulphur dioxide and oxygen that the composition of sulphuric acid was first determined by Gay-Lussac. A **basic sulphate** of the composition $Al_2O_3,SO_3,9H_2O$ or $(AlO)_2SO_4,9H_2O$ is found naturally as ALUMINITE, and a crystalline **basic sulphate** of the composition $Al_2O_3,2SO_3$ can be prepared artificially by the action of sulphuric acid on an excess of alumina.

(*b*) **Potash alum,** $KAl(SO_4)_2,12H_2O$, has been known from classical times as a crystalline salt with an astringent taste. It was prepared in Italy by roasting and extracting with water an ALUM ROCK containing ALUNITE, a basic potassium aluminium sulphate,

$$KAl(SO_4)_2,Al(OH)_3,3H_2O,$$

formed by the action of sulphuric acid, *e.g.*, from weathered iron pyrites, on a silicate rock of the felspar type. It can also be prepared by roasting ALUM SHALE, containing iron pyrites and clay; ferrous sulphate and sulphuric acid, formed by oxidation of the pyrites on exposure to air, then act upon the clay to form aluminium sulphate; on adding potash or ammonia, POTASH ALUM, $KAl(SO_4)_2,12H_2O$, or AMMONIA ALUM, $NH_4Al(SO_4)_2,12H_2O$, crystallises out. Alum can also be prepared by the addition of potassium sulphate to aluminium sulphate made by the action of sulphuric acid on bauxite.

(*c*) *Isomorphism of the Alums.*—The most striking property of the alums is their ready crystallisation in large regular octahedra belonging to the cubic system (Figs. 8 and 9, p. 11). A long series of isomorphous alums is known in which the potassium is replaced by univalent elements such as Na, Li, Rb, Cs, Ag, Tl, and the aluminium by chromium, ferric iron, tervalent thallium, rhodium, or iridium; the sulphur can also be replaced by selenium. Crystals of the composition

$KAl(SO_4)_2,4H_2O$ separate slowly when alum is melted in its water of crystallisation; in some cases (*e.g.*, the tervalent earths) these lower hydrates are the only alums which are known.

(*d*) *Mordants and Lakes.*—Alum is used very largely in dyeing, especially for cotton fabrics, which will only retain certain dyes when impregnated with a basic material such as aluminium hydroxide or with an acid material such as stannic acid or tannic acid. These substances, which are added to the fibre to retain the colouring matter, are known as MORDANTS. Silk and wool already contain acid and basic groups to which the basic or acid groups of the dye-stuff can attach themselves, and can therefore be dyed without a mordant. Precipitated alumina is also used very largely in the manufacture of pigments, in order to fix colouring matters which are soluble in water and which would therefore "run" unless retained by an acid or basic precipitate; pigments of this type are generally described as LAKES.

Aluminium Silicates.

The alumino-silicates of the alkali metals, etc., have already been described amongst the mineral silicates in Chapter XXIX (p. 502), as well as amongst the natural compounds of aluminium (p. 652). A double silicate of sodium and aluminium containing sulphur and possessing a beautiful blue colour has long been known as the mineral LAPIS LAZULI; a similar product is prepared artificially by heating clay with sodium sulphate and carbonate, charcoal and sulphur, and is sold as a blue pigment under the name of ULTRAMARINE. The nature of the coloured compound is not known definitely, but it has been formulated as $3NaAlSiO_4,Na_2S_2$. The principal silicates in which aluminium is the only metal are set out below.

(*a*) **Aluminium monosilicate,** Al_2O_3,SiO_2 or Al_2SiO_5, is a trimorphous compound, occurring in three mineral forms as follows:—

Mineral.	*Crystalline System.*	*Density.*	*Hardness.*
ANDALUSITE .	Orthorhombic	3·18	7·5
SILLIMANITE .	,,	3·2	6 to 7
CYANITE . .	Asymmetric	3·6	7

The most stable form is SILLIMANITE, into which andalusite and cyanite are changed by heating to about 1350°. Pure artificial sillimanite melts at 1816°.

It has been suggested that these three forms of aluminium silicate differ in molecular structure, *e.g.*, that cyanite, which is especially resistant to the action of acids, may be an aluminyl metasilicate, $(AlO)_2SiO_3$, sillimanite a basic orthosilicate, $(AlO)AlSiO_4$, compare $NaAlSiO_4$, and andalusite a polymeride, $(AlO)_3(AlSiO_4)_3$, since when heated with potassium carbonate and fluoride at 250° it is converted into the mica known as muscovite, $KH_2(AlSiO_4)_3$. These formulæ are, however, speculative.

TOPAZ, $Al_2F_2SiO_4$ (Fig. 242), differs from the three preceding minerals in that one atom of oxygen has been replaced by two atoms of fluorine ; it

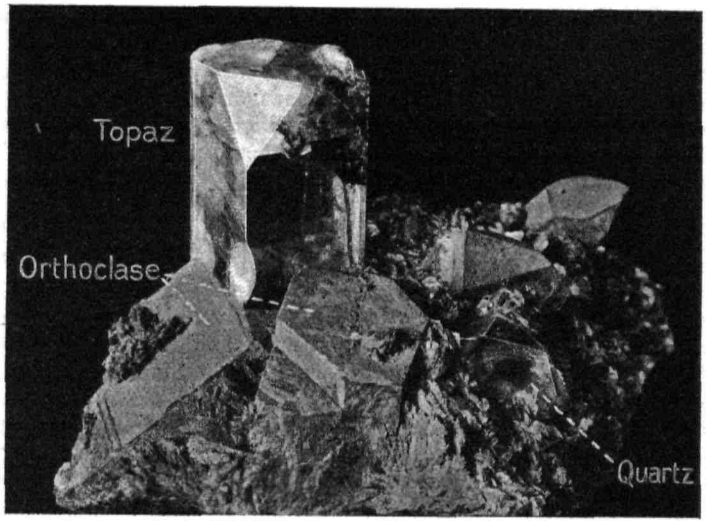


FIG. 242.—ALUMINIUM SILICATES. (British Museum, Natural History.)
The figure shows a crystal of topaz $(AlF_2)AlSiO_4$, with orthoclase or potash-felspar, $KAlSi_3O_8$, and quartz.

may be formulated as an orthosilicate, $(AlF_2)AlSiO_4$, compare $NaAlSiO_4$, or both compounds may be formulated as metasilicates,

$$\underset{\text{Topaz.}}{(AlF_2)(AlO)SiO_3}, \text{ compare } \underset{\text{Nephelite.}}{Na(AlO)SiO_3} \text{ and } \underset{\text{Cyanite.}}{(AlO)_2SiO_3}.$$

(*b*) **Aluminium disilicate,** $Al_2O_3,2SiO_2$, or $Al_2Si_2O_7$, is not known in the free state, but is present in a hydrated form in **aluminosilicic acid,** $HAlSiO_4$, or $Al_2Si_2O_7,H_2O$, a compound which is known as a rare mineral, and which may be regarded as the parent substance from which the alumino-silicates $NaAlSiO_4$ and $Ca(AlSiO_4)_2$ are derived. It is much more abundant in the form of kaolinite, $H_4Al_2Si_2O_9$, which may be written $Al_2Si_2O_7,2H_2O$. When heated, it does not give the anhydrous disilicate, but a mixture of the monosilicate with free silica,

$$H_4Al_2Si_2O_9 = Al_2SiO_5 + SiO_2 + 2H_2O;$$

sillimanite, the stable form of the monosilicate, is therefore a normal constituent of the hard porcelain prepared from kaolinite (see below). Kaolinite when heated with sulphuric acid forms aluminium sulphate and silica. A soluble product is also obtained by fusing it with alkalies, which convert it into the aluminate and silicate of the alkali ; the analogous changes which take place when clay is converted into Portland cement by the action of lime have already been described (p. 642).

Clay and its Uses.

CLAY is essentially a hydrated aluminium silicate in the form of very minute or "colloidal" particles, with the characteristic properties of being plastic when wet, but of baking to a hard mass when heated strongly. The plasticity is increased by alkalies but is diminished by acids; thus an alkaline clay "slip," *i.e.*, a mixture of clay and water containing a trace of free alkali, may be sufficiently plastic to be cast into a mould; on the other hand, the addition of acids causes the suspended particles of the "slip" to coagulate and diminishes or destroys its plasticity. Clay which has been dried at 100° recovers its plasticity when wetted; but if heated to 500° the hydrogen silicates are decomposed with loss of water and the clay will not become plastic again; clay is therefore frequently burnt to prevent its slipping down into railway cuttings, the "burnt ballast" being freely permeable to water and no longer plastic. At about 900° clay begins to sinter through the melting of its more fusible constituents; in this process it shrinks and becomes hard and stony; the shrinkage can be diminished by mixing the clay with fragments of "grog" or material which has already been burnt. At higher temperatures the clay becomes vitreous and then melts, the maximum temperature for complete melting being the melting-point of pure sillimanite at 1816°.

The typical clay consists chiefly of kaolinite formed by the weathering of felspar,

$$2KAlSi_3O_8 + 2H_2O + CO_2 = H_4Al_2Si_2O_9 + 4SiO_2 + K_2CO_3;$$

but as it is usually derived from granite or other complex igneous rocks, it also contains particles of quartz, felspar, and mica, in addition to the silica shown in the preceding equation, which may be carried away in combination with the alkali. Clays which are still in the position in which they were first produced are known as RESIDUAL CLAYS, and usually show a gradual transition from pure clay to undecomposed rock. Clays which have been washed away by water and deposited elsewhere are known as SEDIMENTARY CLAYS; these may become hardened to SHALE or SLATE, and if mixed with chalk are described as MARL.

(*a*) *China Clay*.—Residual clays which are free from iron, and therefore white, are known as CHINA CLAY, and are used in the manufacture of PORCELAIN. This is prepared by igniting a finely-ground natural or artificial mixture of kaolin and quartz with a FRITT containing a sufficient quantity of potash or lime, *e.g.*, in the form of felspar or bone-ash, to produce partial fusion in the kiln. A GLAZE is produced on the surface by dipping the porous product (biscuit-ware) into water holding in suspension either pure felspar or a mixture richer in lime than that used for the porcelain "body" and melting this by firing at a higher temperature in the kiln. Ordinary "china" is made in a similar manner, but with a more fusible fritt and

a glaze containing a considerable proportion of borate. Common earthenware is made by heating less pure clays, which are more fusible than china clay; it is glazed either by painting the surface with a compound of lead to form a fusible lead silicate, or by throwing salt into the kiln to produce a fusible sodium alumino-silicate.

China clay is purified by mixing it with water, and allowing the coarser particles to settle, whilst the finer particles are carried forward into settling-tanks where the clay is allowed to dry to a thick paste; it is then dried in kilns and cut into blocks for transport. A much more complete purification can be effected by ELECTRO-OSMOSIS; in this process two electrodes with a potential difference of about 70 volts between them are immersed in a thin cream of clay and water to which sodium silicate has been added; the fine particles of clay pass quickly to the anode and are deposited as a cake containing only 25 per cent. of water, since the water is driven in the opposite direction towards the cathode; the impurities remain suspended in the liquid and are carried away by the water from which the clay has been removed. By making the anode in the form of a rotating drum dipping into the liquid almost to the axis, whilst the cathode is a half-cylinder of coarse gauze below it, the purification of the clay can be carried out on a commercial scale. The product is more refractory than the unpurified clay and is particularly suitable for use as fireclay of the highest grade.

(*b*) *Fireclay.*—For making crucibles, retorts, fire-bricks and furnace-linings, which must resist a temperature of 1500° without softening, a FIRECLAY is used which is rich in silica and alumina and comparatively free from the oxides of magnesium, calcium, iron, sodium, and potassium. The principal deposits of fireclay are shales, or hardened sedimentary clays, underlying the coal measures; these become soft and plastic on exposure to air. The common clays used for making bricks are usually sedimentary clays coloured with oxides of iron, which give a red colour to the bricks if more than 4 per cent. Fe_2O_3 is present; hardened clays which become plastic on weathering are now used for this purpose as well as the softer surface clays.

Detection and Estimation of Aluminium.

Aluminium does not give a flame spectrum, but the metal gives a characteristic arc spectrum which is particularly rich in ultra-violet lines.

In qualitative analysis, aluminium is precipitated as **aluminium hydroxide,** $Al(OH)_3$, by a mixture of ammonia and ammonium chloride, after throwing down metals the sulphides of which are insoluble in acids. Aluminium hydroxide can be separated from chromium hydroxide and ferric hydroxide by its solubility in an excess of alkali. If an oxidising agent such as bromine is added to the solution after making it strongly alkaline, only the iron is thrown down, the chromium being retained in solution as a chromate; on acidifying with nitric acid and adding ammonia, aluminium is precipitated as hydroxide; the chromium can then be precipitated as barium chromate. When heated on charcoal

with a soluble salt of cobalt, aluminium compounds give a bright blue product.

In quantitative analysis aluminium is precipitated as hydroxide and converted into **aluminium oxide,** Al_2O_3, by ignition.

The atomic weight of aluminium is based upon determinations of the weight of alumina left on igniting ammonia alum,

$$2NH_4Al(SO_4)_2,12H_2O = Al_2O_3 + 2NH_3 + 4SO_2 + 2O_2 + 25H_2O,$$

on exact determinations of the ratio $AlBr_3 : 3Ag$, and on determinations of the ratio $Al : 3H$ by measuring the hydrogen liberated by the action of caustic soda on aluminium.

The Elements of the Rare Earths.

Classification.

The elements of the "rare earths" are a group of metals which are associated together in nature, and resemble one another so closely that they cannot be separated by the ordinary chemical processes of selective precipitation, *e.g.*, as used in qualitative analysis. Tedious processes of fractional crystallisation or precipitation result, however, in a gradual separation of the elements, the progress of which can be checked by measuring the equivalent, or by observing the physical properties, *e.g.*, the absorption spectra, of the various fractions. The components of the various fractions have now been identified by *X*-ray analysis (p. 535), and atomic numbers have been assigned to them which form a consecutive series from 57. La to 71. Lu, with a single gap for an unknown element of atomic number 61. The rare-earth elements are conveniently grouped as follows :—

Table 73.—Classification of the Elements of the Rare Earths.

Included in the *Yttrium group*		21. Scandium	Sc =	45·1
		39. Yttrium	Yt =	89·33
(*a*) *Cerium group.*		57. Lanthanum	La =	139·0
		58. Cerium	Ce =	140·25
		59. Praseodymium	Pr =	140·9
		60. Neodymium	Nd =	144·3
		62. Samarium	Sa =	150·4
(*b*) *Yttrium group.*	Terbium sub-group.	63. Europium	Eu =	152·0
		64. Gadolinium	Gd =	157·3
		65. Terbium	Tb =	159·2
	Erbium sub-group.	66. Dysprosium	Ds =	162·5
		67. Holmium	Ho =	163·5
		68. Erbium	Er =	167·7
		69. Thulium	Tm =	168·5
	Ytterbium sub-group.	70. Ytterbium	Yb =	173·5
		71. Lutecium	Lu =	175·0.

The quadrivalent element thorium (p. 680) is commonly associated with the rare earths, and shows many points of similarity, especially to cerium. It is therefore often classified with the elements of this group. Thus when the earths are divided according to the solubility of their double sulphates in a saturated solution of potassium sulphate, they fall into three groups as follows :

Insoluble. Cerium group 57–62 with 21. Scandium and 90. Thorium.
Slightly soluble. Terbium sub-group 63–65.
Soluble. Erbium and Ytterbium sub-groups 66–71 with 39. Yttrium.

Occurrence.

The first of the rare earths was discovered by Gadolin in 1794 at Ytterby, in a mineral now called gadolinite, and was described as YTTRIA. CERIA was discovered in 1803, but both earths were found to be complex mixtures ; thus the cerium group now contains 5 elements, and the yttrium group includes 10 elements.

The principal source of the CERIUM EARTHS at the present time is the mineral MONAZITE, an orthophosphate of the type [Ce, La, etc.] PO_4, containing also thorium dioxide and silica. This mineral is worked in order to produce salts of thorium and cerium for the manufacture of incandescent gas mantles, and large quantities of the other rare earths are produced as by-products. The mineral is also present in MONAZITE SAND, which is found in Brazil as a river and seashore sand, and in Travancore as monazite sand-beds. These sands contain about 2 per cent. of monazite mixed with other heavy minerals, such as rutile, ZrO_2, thorite, $ThSiO_4$, cassiterite, SnO_2, magnetite, Fe_3O_4, quartz, SiO_2, and topaz, $(AlF_2)AlSiO_4$.

The YTTRIUM EARTHS are, as a rule, present only in small quantities in monazite, but yttrium is found as an orthophosphate, $YtPO_4$, in XENOTIME, a mineral which is isomorphous with thorite, $ThSiO_4$, etc.

Almost all the rare-earth minerals contain thoria, and conversely THORIANITE, ThO_2,U_3O_8, which is one of the principal sources of thorium (p. 680), contains from 12 to 25 per cent. of cerium earths.

Separation of the Rare Earths.

In order to separate the rare earths, the mineral, which must be very finely ground, is digested with hot concentrated hydrochloric or sulphuric acid, or fused with sodium hydrogen sulphate to convert the earths into sulphates, and dissolved in water. Thorium, which belongs to a different group of elements, can be precipitated from the solution by the addition of sodium thiosulphate, which throws down a mixture of **thorium hydroxide,** $Th(OH)_4$, and sulphur. The oxalates of the cerium group are then precipitated by adding a warm solution of ammonium oxalate, filtered off, and converted into hydroxides. The hydroxides are suspended in a solution of sodium hydroxide and acted on by a rapid current of chlorine for some hours, when the cerous hydroxide, $Ce(OH)_3$, is oxidised to **ceric hydroxide,** $Ce(OH)_4$, which remains

undissolved, whilst the other hydroxides pass into solution as chlorides. The remaining earths must be separated by fractional crystallisation, precipitation, etc. The principal compounds used for this purpose are set out below.

(i) *Sulphates*, such as **neodymium sulphate** $Nd_2(SO_4)_3,8H_2O$, which are much less soluble in hot than in cold water, and are therefore precipitated when an ice-cold saturated solution is heated to the boiling-point.

(ii) *Double Sulphates*, such as **potassium cerium sulphate**, $Ce_2(SO_4)_3,3K_2SO_4$, or $K_3Ce(SO_4)_3$, which is precipitated with other sulphates of the cerium group from a boiling solution by the addition of potassium sulphate.

(iii) *Nitrates, e.g.*, **gadolinium nitrate**, $Gd(NO_3)_3,6H_2O$, which is less soluble in nitric acid than any other nitrate of the series.

(iv) *Double Ammonium Nitrates, e.g.*, **ammonium ceric nitrate**, $(NH_4)_2Ce(NO_3)_6$, which serves for the preparation of pure cerium salts, and **ammonium lanthanum nitrate**, $(NH_4)_2La(NO_3)_5,4H_2O$, which has been used for the separation of lanthanum.

(v) *Double Magnesium Nitrates* and *Double Nickel Nitrates, e.g.*, **magnesium neodymium nitrate**, $Mg_3Nd_2(NO_3)_{12},24H_2O$, which has been used to separate neodymium from praseodymium, and **nickel gadolinium nitrate**,

$$Ni_3Gd_2(NO_3)_{12},24H_2O,$$

which has been used for the final separation of gadolinium and terbium. Gadolinium has also been separated by crystallising out **magnesium gadolinium nitrate**, $Mg_3Gd_2(NO_3)_{12},24H_2O$, in solid solution with the isomorphous **magnesium bismuth nitrate**, $Mg_3Bi_2(NO_3)_{12},24H_2O$.

(vi) *Bromates*, which are of value in separating yttrium and the elements of the yttrium group, the bromates increasing in solubility from 62. Samarium to 70. Ytterbium. Yttrium itself (39) is placed between 67. Holmium and 68. Erbium in this series.

(vii) *Organic Compounds* of many types have also been used in the separation of the rare earths.

Other methods of separation depend (i) on the fractional decomposition of the nitrates whereby the least basic earths are rendered insoluble; (ii) on fractional precipitation with bases of various strengths, *e.g.*, ammonia, organic bases such as aniline, the caustic alkalies, magnesia, cuprous oxide, or some of the rare earths themselves; (iii) on fractional precipitation of oxalates from the nitrates, of neutral chromates from the dichromates, etc.

Properties of the Elements of the Rare Earths.

(*a*) *Properties of the Metals.*—The elements of the rare earths are metals, although only those of the cerium group have been prepared in a pure state. An alloy of cerium-metals with iron is, however, used under the name of MIXED-METAL in cigarette lighters to produce sparks for the ignition of tinder or petrol.

The metals of the cerium group burn brightly when heated in oxygen at about 250° and combine with hydrogen and nitrogen to form compounds of the type LaH_3 and LaN; they decompose water and dissolve readily in dilute acids. Like aluminium they form insoluble hydroxides,

fluorides, phosphates, and oxalates, but soluble deliquescent chlorides, sulphates, and nitrates. All the rare earth metals give characteristic line spectra when their compounds are heated in a carbon arc, and the coloured salts when dissolved in water give characteristic absorption spectra.

A notable feature of these elements is the relative constancy of the physical properties of successive elements, in marked contrast to the steep gradation shown in other parts of the periodic table.

TABLE 74.—PROPERTIES OF THE ELEMENTS OF THE RARE EARTHS.

Atomic Number	39	57	58	59	60	62	70
Element	Yt	La	Ce	Pr	Nd	Sa	Yb
Atomic Volume	23·3	22·6	20·3	21·8	20·7	19·5	19·8
Melting-point	—	810°	635°	940°	840°	1300 to 1400	—

The solubilities of the oxalates of these seven elements range from 0·4 to 3·3 mg. per litre, and the solubilities of the five double magnesium nitrates of the cerium group in weak nitric acid range only from 0·04 to 0·06 mol. per litre.

(*b*) *Valency.*—The elements of the group all form tervalent compounds, but cerium is peculiar in that it also forms quadrivalent compounds, like thorium, and can therefore be separated from the other elements of the group, almost as readily as thorium, by oxidation to the quadrivalent hydroxide. Bivalent chlorides, $SaCl_2$ and $EuCl_2$ (compare indium dichloride, $InCl_2$), have also been prepared from the two elements 62. Samarium and 63. Europium, which end the cerium group and begin the yttrium group of elements.

(*c*) *Isomorphism.*—In view of the fact that scandium and yttrium and the cluster of rare earths from lanthanum to lutecium are tervalent elements analogous to aluminium, it is remarkable that double sulphates of the type of the alums are not known. Thus cerium forms the double sulphates represented by the formulæ $NaCe(SO_4)_2,H_2O$, and $(NH_4)Ce(SO_4)_2$, both anhydrous and with 1 or $4H_2O$. No compounds with $12H_2O$ are known, although sulphates of the type $KAl(SO_4)_2,4H_2O$ and $NH_4Al(SO_4)_2,4H_2O$ have been prepared from the common alums by fusion at 86°. Another notable difference between the salts of the rare earths and the tervalent salts of aluminium, chromium, and iron is that whereas in the latter the tervalent metal is commonly associated with a single atom of the alkali metal, as in

Felspar,	$KAlSi_3O_8$,
Alum,	$KAl(SO_4)_2,12H_2O$,
Glauconite,	$KFeSi_2O_6$,
Soluble Prussian blue,	$KFe(FeC_6N_6)$, etc.,

the rare earths frequently form double salts containing equivalent quantities of the tervalent rare-earth element and of the univalent or

bivalent metal with which it is associated. Thus cerium forms an **acid sulphate** of the formula $H_3Ce(SO_4)_3$ and an anhydrous **potassium cerous sulphate** of the formula $K_3Ce(SO_4)_3$, instead of compounds of the type $KCe(SO_4)_2,12H_2O$; these salts may therefore be compared with the double sulphates $KHSO_4$, $K_2Mg(SO_4)_2,6H_2O$, $K_3Ir(SO_4)_3,H_2O$, $K_4Th(SO_4)_4,2H_2O$. The same tendency is seen in the double nitrates of the type $M_3Ce_2(NO_3)_{12},24H_2O$, where M = Mg, Mn, Co, Ni or Zn, as well as in the analogous bismuth compounds such as $Mg_3Bi_2(NO_3)_{12},24H_2O$, which contain six equivalents each of the bivalent and tervalent metal ; the double alkali-nitrates of the rare earths are, however, of a different type (see below).

Isomorphism has been recorded in the following series :—

(i) *Sulphates :* Yttrium sulphate, $Yt_2(SO_4)_3,8H_2O$, and seven rare earth sulphates from 59. Praseodymium to 70. Ytterbium, but excluding the sulphates of 21. Scandium, 57. Lanthanum, and 58. Cerium, which crystallise in other forms.

(ii) *Ethyl Sulphates :* $La(SO_4Et)_3,9H_2O$ (where Et = C_2H_5), and the corresponding compounds of all the rare-earth elements from 57. Lanthanum to 70. Ytterbium.

(iii) *Double Nitrates.*

$Na_2M(NO_3)_5,H_2O$	where M = 57. La,	58. Ce,	59. Pr,	60. Nd.	
$(NH_4)_2M(NO_3)_5,4H_2O$	,, M = 57. La,	58. Ce,	59. Pr,	60. Nd.	
$Mg_3M_2(NO_3)_{12},2H_2O$	,, M = 57. La,	— —,	59. Pr,	60. Nd,	
	62. Sa,	— —,	64. Gd, or 83. Bi,		

and Mg may be replaced by Mn, Ni, Co, or Zn.

Elements and Compounds of the Rare Earths.

21. *Scandium,* Sc = 45·1.—The properties of scandium, under the name of EKABORON, were predicted by Mendeléef in 1871, and his predictions were verified by the discovery of the element by the Scandinavian chemist Nilson in 1879. The rare earths which are left behind when wolframite is fused with soda and extracted with water to dissolve out sodium tungstate (p. 747) consist mainly of scandium, which can be separated quite readily from the rare-earth elements of higher atomic weight and from thorium. The metal has not been isolated, but its **oxide,** Sc_2O_3, is the weakest base of the rare earths, although strong enough to form a **carbonate,** $Sc_2(CO_3)_3$. Its salts are colourless and resemble those of aluminium ; but the **sulphate** crystallises with only 5 or 6 molecules of water, forms an **acid sulphate,** $H_3Sc(SO_4)_3$, a sparingly soluble **double potassium sulphate** of the formula $K_3Sc(SO_4)_3$ (compare cerium), and an anhydrous **ammonia alum,** $NH_4Sc(SO_4)_2$.

39. *Yttrium,* Yt = 89·33.—Yttrium was the first of the rare earths to be discovered, the crude earth being separated from " gadolinite " by Gadolin in 1794. The metal is a grey powder which oxidises readily in air and is converted into the hydroxide by boiling water. **Yttrium oxide,** Yt_2O_3, although a weaker base than lanthanum oxide, is stronger than the other members of the " yttrium " group of rare earths from 63. Europium to 71. Lutecium, *e.g.*, it absorbs carbon dioxide from the air and expels ammonia from ammonium salts. The oxide is colourless and yields colourless tervalent salts of the usual type.

(a) *Cerium Group.*

57. *Lanthanum*, La = 139·0.—This element (Greek λανθάνω, I lie hidden) was separated from cerium in 1839. The oxide is the strongest base of this family of elements; thus it turns litmus blue, absorbs carbon dioxide from the air, liberates ammonia from ammonium salts, and slakes like quicklime when moistened with water. The oxide and its salts are colourless. Metallic lanthanum, prepared by the electrolysis of a fused mixture of the chloride with KCl,NaCl and $BaCl_2$, is an iron-grey metal of density 6·1, which melts at 810°; it can be hammered into foil and drawn into wire; it takes a bright polish, but tarnishes even in dry air. It burns to the **oxide**, La_2O_3, and **nitride**, LaN, when heated in air, and gives bright sparks like iron powder in a Bunsen flame. It takes fire in chlorine and burns to the **chloride**, $LaCl_3$, combines with incandescence when heated in hydrogen at 240°, forming the **hydride**, LaH_3, and decomposes hot water, liberating hydrogen and forming the **hydroxide**, $La(OH)_3$. The **carbide**, LaC_2, is formed by reducing the oxide with charcoal and gives a mixture of acetylene with some methane and ethylene when decomposed by water. The salts are of the usual type and do not give any absorption spectrum in solution.

58. *Cerium*, Ce = 140·25.—Ceria was discovered in 1803 as a mixture of earths from which the five elements of the cerium group were afterwards separated. It is the most important of the rare earths, since it is the only one which has found an extensive commercial use. It is an essential constituent of incandescent gas mantles, which contain about 1 per cent. of ceria with 99 per cent. of thoria. For this reason minerals containing ceria have been mined and worked on a very extensive scale, with the result that the other rare earths which are associated with it are now available in very large quantities. An outlet for these superfluous earths has been found in the use of the mixed metals for igniting tinder, and of the mixed fluorides for increasing the luminosity of carbon arcs.

Cerium differs from all the other rare earths in giving both tervalent and quadrivalent compounds, and it is perhaps to this variable valency that it owes its unique value in the incandescent mantle. It will be noticed that if the rare earths were distributed, as Mendeléef supposed, in consecutive columns of the periodic table, cerium would occupy a place in the table in Column IV between zirconium and thorium; its dual properties therefore appear to correspond with the two positions in which it might be placed in the table.

Ingots of **metallic cerium** weighing about a pound have been prepared by electrolysing molten anhydrous **cerous chloride**, $CeCl_3$, with a little sodium and potassium chloride, in an iron crucible which acts as the cathode, whilst the chlorine is set free at a carbon anode (Fig. 243). The metal is freed from oxide and carbide, and from metallic iron, by dissolving it in mercury, skimming off the impurities, and distilling off the mercury in a high vacuum. The density of the metal is 6·9. It melts at 635°, but oxidises very readily when cast and is also liable to pick up iron from the mould. It is a soft metal which can be rolled into thin sheets and cut readily with a knife or scissors,

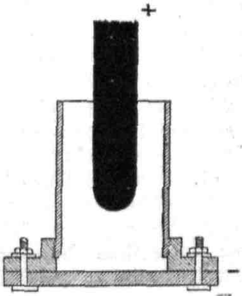


FIG. 243.—CRUCIBLE FOR PREPARATION OF CERIUM.

but some of its alloys are so brittle as to give off a spray of minute particles when struck with a file, and are used in artificial sparking devices. Metallic cerium liberates hydrogen slowly from boiling water and dissolves readily in dilute acids. It burns brightly when heated to 160° in air, or to 215° in chlorine or in bromine-vapour. It unites without luminosity when heated in hydrogen at 345° or in nitrogen at 1000°, but can also be made to burn with brilliant incandescence in nitrogen.

The tervalent cerous salts are colourless compounds of the normal type and need not be described in detail. **Cerous oxide**, Ce_2O_3, has been prepared by heating the hydroxide in an inert atmosphere, and by reducing the dioxide with calcium; it cannot be prepared by burning the metal in air or oxygen, nor by heating the oxide, nitrate, carbonate, or hydroxide, since these processes give cerium dioxide. **Cerium dioxide,** CeO_2, is colourless like the sesquioxide, but becomes yellow when heated. When dissolved in sulphuric acid it forms **ceric sulphate,** $Ce(SO_4)_2$, from which a **hydrate,** $Ce(SO_4)_2,4H_2O$, and **double sulphates** such as $K_4Ce(SO_4)_4,2H_2O$, can be prepared. Ceric sulphate oxidises nitrites quantitatively to nitrates and is thereby reduced to cerous sulphate as shown in the equation

$$2Ce(SO_4)_2 + KNO_2 + H_2O = Ce_2(SO_4)_3 + KNO_3 + H_2SO_4.$$

Ceric hydroxide, $Ce(OH)_4$, can be prepared by the addition of ammonia to ceric sulphate or by oxidation of cerous hydroxide in the air; it has also been prepared in a gelatinous form like silicic acid, but does not possess any acid properties. When dissolved in nitric acid it gives a quadrivalent **ceric nitrate,** which can be isolated in the form of double salts such as $(NH_4)_2Ce(NO_3)_6$; **ceric chloride** also is known only in the form of double salts, derived from $(NH_4)_2CeCl_6$ by using organic bases in place of ammonia. An **oxychloride,** $CeOCl_2,H_2O$, has been prepared.

59. *Praseodymium,* Pr = 140·9. 60. *Neodymium,* Nd = 144·3.—These two elements were separated from lanthanum in 1841 and were described as a single element under the name of DIDYMIUM (Greek, δίδυμος, twofold or twin) on account of their close similarity to the elements from which they had been separated; the two elements praseodymium and neodymium (Greek, πράσιος, leek-green; νέος, new) thus included in a single twin were only separated from one another in 1885. Their properties are in general those of the cerium group, but they are remarkable for forming green and red salts respectively, which exhibit characteristic absorption spectra in solution. Praseodymium also resembles cerium in forming a **dioxide,** PrO_2, when the nitrate is heated with potassium nitrate at 450°; but it is less stable than the sesquioxide, and no salts have been prepared from it. It is suggested that the properties of these two elements, like those of cobalt and nickel, are in the inverse order of their atomic weights.

62. *Samarium,* Sa = 150·4.—Samarium, which is associated with the earths of the terbium sub-group as well as with those of the cerium group, is noteworthy because it forms bivalent salts such as $SaCl_2$ and SaI_2, which are even less stable than the corresponding bivalent chromous salts (p. 737). The tervalent salts are yellow and give a characteristic absorption spectrum.

(b) *Terbium Sub-group.*

63. *Europium,* Eu = 152·0.—Europium, like samarium, gives a bivalent chloride, $EuCl_2$, but this can be dissolved in water without change. The

tervalent salts are rose-coloured and show a weak absorption spectrum ; the arc-spectrum is, however, very bright and characteristic and serves for the detection of small traces of the element.

64. *Gadolinium*, Ga = 157·3.—Gadolinium forms a colourless oxide, Ga_2O_3, and colourless tervalent salts which show absorption bands only in the ultra-violet. The oxide is magnetic and gives the least soluble nitrate of the series, so that the element is less difficult to separate than many of the others.

65. *Terbium*, Tb = 159·2.—Terbium forms a colourless oxide which, like those of the adjacent elements gadolinium and dysprosium, is strongly magnetic ; its salts are colourless, but show absorption bands in the blue and ultra-violet. A brown **peroxide,** to which the formula Tb_4O_7 has been assigned, has also been prepared.

(c) *Erbium Sub-group.*

66. *Dysprosium*, Ds = 162·5. 67. *Holmium*, Ho = 163·5.
68. *Erbium*, Er = 167·7. 69. *Thulium*, Tm = 168·5.

Dysprosium is notable for its magnetic properties and for the yellow colour and absorption spectra of its salts. Holmium also gives yellow salts. Erbium, the most plentiful of the yttrium earths after yttrium itself, forms a rose-red oxide and red salts. Thulium forms a colourless oxide and green salts.

(d) *Ytterbium Group.*

70. *Ytterbium*, Yb = 173·5. 71. *Lutecium*, Lu = 175·0.

Ytterbium and lutecium form colourless oxides and colourless salts ; they represent two fractions from a mixture formerly described as ytterbium, the third fraction, " celtium," having been shown by *X*-ray analysis to contain no new element.

TABLE 75.—SALTS OF THE RARE EARTHS.

		Tervalent Salts.	*Other Compounds.*	*Coefficient of Magnetisation.*
Cerium Group.	57. La	—	—	— 0·2
	58. **Ce**	—	CeO_2 etc.	—
	59. Pr	Green	PrO_2	—
	60. Nd	Red	—	—
	62. Sa	Pink	$SaCl_2$	+ 6
Terbium Sub-group	63. Eu	Rose-red	$EuCl_2$	+ 33
	64. Gd	—	—	+161
	65. **Tb**	—	Tb_4O_7	+237
Erbium Sub-group	66. Ds	Yellow	—	+290
	67. Ho	Yellow	—	—
	68. **Er**	Red	—	—
	69. Tm	Green	—	—
Ytterbium Sub-group.	70. **Yb**	—	—	—
	71. Lu	—	—	—

The properties of the salts of the rare earths are summarised in Table 75.

(i) The colours of the tervalent salts are arranged almost symmetrically. The first two and the last two elements give colourless salts ; the two groups

of coloured salts then show a progressive displacement of the principal absorption of light from the red to the violet end of the spectrum, until finally the two elements in the middle of the series 64. Gd and 65. Tb show strong absorption bands in the ultra-violet region, but have no visible colour.

(ii) Two elements, 62. Sa and 63. Eu, form bivalent chlorides; two elements, 59. Pr and 65. Tb, placed symmetrically on either side of them form peroxides; one element, namely, cerium, gives not only a peroxide, but also a series of quadrivalent salts corresponding with those of thorium.

(iii) Three elements, 64, 65, and 66, show strong magnetic properties in all their compounds; these three elements are the ninth, tenth, and eleventh elements of Period VI, and correspond with the magnetic elements iron, cobalt, and nickel in Period IV; in each case the special magnetic properties of the triad disappear on passing to the twelfth element of the period.

CHAPTER XXXV

THE HOMOLOGUES OF CARBON

TITANIUM, ZIRCONIUM AND THORIUM, GERMANIUM, TIN AND LEAD

Atomic Number.	*Element.*	*Symbol.*	*Atomic Weight.*
22	Titanium	Ti	48·1
40	Zirconium	Zr	90·6
72	—	—	—
90	Thorium	Th	232·15
32	Germanium	Ge	72·5
50	Tin	Sn	118·7
82	Lead	Pb	207·20

Classification.

The quadrivalent elements carbon and silicon, which are the central elements of the two short periods of Mendeléeff's classification, are distinct in every respect from the "transition-elements" which occupy the centres of the subsequent long periods. They are, however, related very closely to a group of quadrivalent elements,

22. *Titanium*, 40. *Zirconium*, 90. *Thorium*,

immediately following the aluminium group, and to a group of quadrivalent elements,

32. *Germanium*, 50. *Tin*, 82. *Lead*,

immediately preceding the nitrogen, oxygen, and halogen families which terminate both the short and the long periods. These quadrivalent elements show a marked relationship to silicon and a more distant relationship to carbon, the first (and the least typical) member of this family. Of the six elements shown above (the element of atomic number 72 being still unknown), only tin and lead are of sufficient importance to demand detailed description; the others are mentioned only in brief introductory paragraphs.

Physical Properties of the Group.

TABLE 76.—PHYSICAL PROPERTIES OF THE QUADRIVALENT METALS.

(a) *Densities.*				(b) *Melting-points.*		(c) *Boiling-points.*
	C 2·25 (graphite)			C 4000° ?		C 3600° ?
	Si 2·5 (metallic)			Si 1420°		Si in arc
Ti 4·5	Ge 5·46			Ti about 1800°	Ge 958°	Ge —
Zr 6·4	Sn 7·28			Zr —	Sn 232°	Sn 2270°
— —	Pb 11·34			— —	Pb 327°	Pb 1525°
Th 11·0				Th about 1700°		

The increase of density with rising atomic weight, which has already been noted in other cases, is again shown in the high densities of lead (11·34) and thorium (11·0); but whereas the high melting-point of silicon (above 1400°) is more than maintained in the series Ti, Zr, Th, there is a marked fall in the series Ge, Sn, Pb, the last two elements being metals of low melting-point from which solders and fusible alloys are made.

Valency.

(*a*) *Quadrivalent Compounds.*—The typical compounds which link together this group of elements are quadrivalent; thus, each member of the group forms a *dioxide* corresponding with silica, SiO_2, and a series of *double fluorides*, corresponding with, and in some cases isomorphous with, the silicifluorides such as K_2SiF_6. Quadrivalent *chlorides* are also known in each case, corresponding with silicon tetrachloride, $SiCl_4$; several of these resemble the chlorides of carbon and silicon in being liquids of low melting-point and boiling-point as shown in the following table, but zirconium and thorium form solid, salt-like, chlorides.

TABLE 77.—PROPERTIES OF QUADRIVALENT CHLORIDES.

Substance.	*Formula.*	*Melting-point.*	*Boiling-point.*
Carbon tetrachloride	CCl_4	− 24°	+ 77°
Silicon tetrachloride	$SiCl_4$	− 89°	+ 58°
Titanium tetrachloride	$TiCl_4$	− 25°	+136°
Germanium tetrachloride	$GeCl_4$	*below* −*100°*	+ *86°*
Zirconium tetrachloride	$ZrCl_4$	solid	?
Stannic chloride	$SnCl_4$	− *33°*	+*114°*
Plumbic chloride	$PbCl_4$	− *15°*	(*decomposes*)
Thorium tetrachloride	$ThCl_4$	+820°	+900°

In all these compounds the quadrivalent element acts as the "positive" or metallic constituent. An interesting link joining silicon to tin and lead is found in their compounds with magnesium, in which the quadri-

valent element appears to act as the "negative" constituent. The three compounds

	Melting-point.
Magnesium silicide, Mg_2Si	1102°
Magnesium stannide, Mg_2Sn	783°
Magnesium plumbide, Mg_2Pb	551°

are stable compounds of high melting-point, which form eutectics with both of their components, and give rise to **W**-shaped freezing-point curves (p. 186) in which the formation of a chemical compound is indicated by a very striking "hump."

(*b*) *Bivalent Compounds.*—The elements of this group also form bivalent compounds, *e.g.*, chlorides such as $TiCl_2$, $GeCl_2$, $SnCl_2$, $PbCl_2$. In the series *titanium, zirconium,* and *thorium*, this tendency diminishes as the atomic weight increases, and bivalent compounds of zirconium and thorium are almost unknown. In the series *germanium, tin,* and *lead*, on the other hand, the bivalent compounds become more important as the atomic weight increases; thus, with the single exception of the dioxide, PbO_2, the quadrivalent compounds of lead were almost unknown until the end of the nineteenth century. Titanium is unique amongst the elements of this series in giving also an important series of tervalent compounds.

(*c*) *Variable Valency.*—This group of elements includes two interesting examples of variable valency, in the cases of

(i) *Titanium*, which can change readily from the tervalent to the quadrivalent condition, or conversely, as in

Titanium trichloride, $TiCl_3$,
Titanium tetrachloride, $TiCl_4$.

(ii) *Tin*, which can be "oxidised" from the stannous to the stannic state or "reduced" from the stannic to the stannous state, as in

Stannous chloride, $SnCl_2$,
Stannic chloride, $SnCl_4$.

Owing to the greater stability of the quadrivalent compounds of these elements, both titanium trichloride and stannous chloride can be used as REDUCING AGENTS, *e.g.*, to remove chlorine from a ferric salt and convert it into a ferrous salt, or to remove chlorine from mercuric chloride and convert it into mercurous chloride or mercury.

$$\underset{\text{Titanium trichloride}}{TiCl_3} + \underset{\text{Ferric chloride}}{FeCl_3} = \underset{\text{Titanium tetrachloride}}{TiCl_4} + \underset{\text{Ferrous chloride}}{FeCl_2}.$$

$$\underset{\text{Stannous chloride}}{SnCl_2} + \underset{\text{Mercuric chloride}}{HgCl_2} = \underset{\text{Stannic chloride}}{SnCl_4} + \underset{\text{Mercury}}{Hg}.$$

Chemical Properties of the Group.

As might perhaps be expected, the two elements titanium and germanium, which are found on the left and right of the transition

elements of the first long period, show a specially close resemblance to silicon; but as the atomic weight increases this resemblance becomes less marked.

(*a*) *First Series.* 22. **Titanium.** 40. **Zirconium.** 90. **Thorium.**—The most notable feature of this series is the progressive disappearance of the acid properties of the dioxides as the atomic weight of the element increases. In thorium dioxide, indeed, the acid properties have disappeared completely and no compounds corresponding with the silicates are known; on the contrary, the dioxide is definitely basic, giving rise to soluble quadrivalent salts, such as the **nitrate,** $Th(NO_3)_4$, and the **sulphate,** $Th(SO_4)_2$, for which no analogy exists in the case of silicon. Thorium is also noteworthy on account of its very close resemblance to the elements of the rare earths.

(*b*) *Second Series.* 32. **Germanium.** 50. **Tin.** 82. **Lead.**—These elements diverge from silicon in a totally different manner. Not only are the quadrivalent compounds more readily reduced to the bivalent state as the atomic weight of the element increases, but even the bivalent oxides part quite readily with their oxygen and are reduced without difficulty to the metallic state. Whilst therefore thorium finds its principal use as the dioxide, tin and lead are industrial metals, which are readily reduced from their ores and have been known and used as metals from a very early period.

22. **Titanium,** Ti = 48·1.

(*a*) *Occurrence.*—Titanium is one of the most abundant of the non-metals, since igneous rocks contain about 0·8 per cent. of titanium dioxide, TiO_2, as compared with 60 per cent. of silica, 2 per cent. of water, 0·5 per cent. of carbon dioxide, 0·3 per cent. of phosphoric oxide, and 0·1 per cent. each of sulphur and fluorine. Titanium therefore replaces silicon in the silicates to the extent of about 2 per cent., but the similarity of the two elements is so great that the presence of titanium is frequently overlooked.

Titanium is segregated most frequently in the form of **ferrous titanate,** or ILMENITE, $FeTiO_3$; this mineral, which is frequently associated with magnetite in igneous rocks, resembles hæmatite very closely in its crystalline form, and was formerly regarded as an isomorphous mixture of two oxides, $[Fe,Ti]_2O_3$; but as it often contains magnesium titanate, $MgTiO_3$, and is isomorphous with manganese titanate, $MnTiO_3$, it is now assumed to be a compound of ferrous oxide with titanium dioxide. In its general appearance ilmenite also resembles thorianite (p. 680), but differs from it in its lower density.

Titanium dioxide, TiO_2, is of interest as a trimorphous mineral. The tetragonal crystals of RUTILE resemble cassiterite, SnO_2 (density 7·0), zircon, $ZrSiO_4$ (density 4·7), and thorite, $ThSiO_4$, in crystalline form, but are of lower density (4·3). ANATASE (density 3·9) is also tetragonal, but its angles and axial ratios are quite different from those of rutile.

BROOKITE (density 4·2) is orthorhombic and is perhaps isomorphous with tridymite, the commonest of the high temperature forms of silica, SiO_2 (density 2·3), but is of higher density. Rutile is the most stable form of titanium dioxide, and pseudomorphs formed by the conversion both of anatase and of brookite into rutile have been found.

(*b*) *Metallic titanium* is very difficult to prepare, since the oxide is very refractory, and the metal unites readily with carbon and nitrogen; thus a blast-furnace product, crystallising in very hard cubes, which was formerly regarded as metallic titanium, has been proved to contain both carbon and nitrogen.

(*c*) *Quadrivalent Compounds.*—These include a liquid **tetrachloride,** $TiCl_4$, freezing at − 25° and boiling at 136° (compare $SnCl_4$), and a **tetrafluoride,** TiF_4, which forms a series of TITANIFLUORIDES, *e.g.*, K_2TiF_6 (compare the silicifluorides, *e.g.*, K_2SiF_6). The amphoteric character of the dioxide is shown more clearly by the formation of a **titanic sulphate,** $Ti(SO_4)_2,3H_2O$, and of a **basic sulphate,** $TiO(SO_4),5H_2O$, in which the titanium dioxide acts as a base, in marked contrast to the TITANATES described above, or prepared by fusing the dioxide with an alkali, in which it acts as the anhydride of an acid. Titanium also forms a quadrivalent **nitride,** Ti_3N_4, prepared by igniting the compound $TiCl_4,4NH_3$, and a quadrivalent **carbide,** TiC, analogous to carborundum, SiC.

(*d*) *Bivalent Compounds.*—The bivalent compounds of titanium include the **monoxide,** TiO (compare SiO), a **monosulphide,** TiS, and a brown **dichloride,** $TiCl_2$, which hisses when thrown into water and liberates hydrogen from it.

(*e*) *Tervalent Compounds.*—Titanium is unique amongst the elements of this group in forming also a full series of tervalent compounds. The violet **trichloride,** $TiCl_3$, is prepared by reduction at a red heat of the vapour of the tetrachloride mixed with hydrogen, or in solution by electrolytic reduction of the tetrachloride in presence of hydrogen chloride. It crystallises from solution as the **hexahydrate,** $TiCl_3,6H_2O$, and forms **double salts** such as $TiCl_3,2CsCl,H_2O$ or Cs_2TiCl_5,H_2O, compare K_2MnF_5,H_2O (p. 757), K_2MnCl_5 and K_2RhCl_5 (p. 820). It is a powerful reducing agent (compare $SnCl_2$) and can be used for the direct titration of ferric salts and of organic nitro-compounds such as trinitrotoluene. The **sesquioxide,** Ti_2O_3, and **sesquisulphide,** Ti_2S_3, have also been prepared, and the tervalent **nitride,** TiN, is actually formed by displacement of oxygen when titanium dioxide is heated in nitrogen.

40. **Zirconium,** Zr = 90·6.

The mineral ZIRCON, $ZrSiO_4$, has already been referred to (p. 678) as being isomorphous with thorite, $ThSiO_4$, with rutile, TiO_2, and with cassiterite, SnO_2, and also as being the first mineral to separate from the liquid magma in the formation of igneous rocks (p. 504).

The **dioxide,** ZrO_2, is even more refractory than silica and is used for making crucibles and furnace linings for work at very high temperatures. It forms a series of ZIRCONATES, *e.g.*, Na_2ZrO_3, and when attacked by carbon and chlorine yields a crystalline **tetrachloride,** $ZrCl_4$ (compare $AlCl_3$), which readily yields basic products. The **tetrafluoride,** ZrF_4, yields a series of ZIRCONIFLUORIDES, *e.g.*, K_2ZrF_6. The basic properties of the dioxide are shown by the formation of a hygroscopic **nitrate,** $Zr(NO_3)_4,5H_2O$, by the action of nitric acid on the hydroxide, and of a soluble **sulphate** of the composition $Zr(SO_4)_2,4H_2O$, by the action of sulphuric acid. Compounds of lower valency are almost unknown.

90. Thorium, Th = 232·15.

(*a*) *Classification.*—Thorium, although showing definite relationships to silicon, titanium, and zirconium, displays an even more remarkable resemblance to the tervalent metals of the rare earths. This resemblance is indeed so striking that cerium, with atomic number 58 (which differs from the other rare-earth elements in forming quadrivalent as well as tervalent compounds), is sometimes included in the thorium family in place of the unknown element of atomic number 72.

This similarity affords another illustration of the "diagonal relationships" to which attention has been directed in connection with other portions of the periodic table of the elements. In this particular case the analogy which exists between the properties of magnesium nitrate, $Mg(NO_3)_2$, cerium nitrate, $Ce(NO_3)_3$, and thorium nitrate, $Th(NO_3)_4$, may be attributed to the combined influence of the increasing valency of the metals, which tends to diminish the basic properties of their oxides, and their increasing atomic weight, which tends to counterbalance this effect by intensifying the basic properties of the oxides.

(*b*) *Occurrence.*—Thorium and its compounds are derived mainly from MONAZITE SAND (p. 667). Its presence in the particles of monazite is perhaps accounted for by the fact that thorium silicate or THORITE, $ThSiO_4$, is isomorphous, not only with zircon, $ZrSiO_4$, but also with the rare-earth phosphate xenotime, YPO_4, which is perhaps typical of the form in which the rare earths are present in monazite. Thorium is also obtained from THORIANITE, a mineral in which the dioxide, ThO_2, is associated with oxides of uranium (p. 749).

(*c*) *Properties and Uses.*—Thorium dioxide or thoria, ThO_2, is used with about 2 per cent. of crude ceria, Ce_2O_3, in INCANDESCENT GAS MANTLES. These are prepared by impregnating cotton fabrics with a mixture of the soluble nitrates of thorium and cerium, drying, burning off in the blowpipe (taking special care to ensure an even shrinkage of the material), and then impregnating the framework of mixed oxides with collodion for safety in transit. The special efficiency of this combination of earths has been attributed to catalytic combustion of the gas of the flame in contact with the mantle; but it is more probably due to the fact that the mantle sends out an unusually small proportion of invisible heat rays and an unusually high proportion of visible light rays.

Metallic thorium, prepared by reducing the chloride with sodium, has a high density (11·0) and burns brightly in air. It resembles the metals of the cerium group in absorbing hydrogen and gives a quadrivalent **hydride,** ThH_4. The **tetrachloride,** $ThCl_4$, is a deliquescent solid which melts at 820° (contrast $TiCl_4$, $GeCl_4$, $SnCl_4$, and $PbCl_4$, which are liquids), and forms a series of hydrates. The **tetrafluoride,** ThF_4, is an insoluble powder (compare CaF_2, CeF_3, etc.), but forms a series of soluble THORIFLUORIDES, such as K_2ThF_6. The **sulphate,** $Th(SO_4)_2$, is a soluble salt which forms **hydrates** with $4H_2O$ and with $9H_2O$ and **double sulphates** such as $K_4Th(SO_4)_4,2H_2O$, which resemble those of magnesium and of the rare earths in containing equivalent quantities of the two metals. **Thorium nitrate,** $Th(NO_3)_4,9H_2O$, is a soluble deliquescent salt, which can also be prepared with $6H_2O$, $5H_2O$, and $2H_2O$; the principal **double nitrates** are of the types $NaNO_3,Th(NO_3)_4,9H_2O$ and $Mg(NO_3)_2,Th(NO_3)_4,8H_2O$, where Na may be replaced by K (the ammonium salt has only $5H_2O$), and Mg by Mn, Co, Ni or Zn.

(*d*) *Radioactivity.*—Thorium, like radium and uranium, which precede and follow it in the periodic classification, possesses the property of radioactivity (see Chapter XLV).

32. **Germanium,** Ge = 90·6.

Germanium resembles silicon, but much less closely than does titanium. Like gallium (Mendeléeff's eka-aluminium), it was discovered in a sulphide ore; Winkler, who found it in ARGYRODITE, $GeS_2,4Ag_2S$, identified it with Mendeléeff's eka-silicon and gave to it the patriotic name Germanium (compare Scandium and Gallium). Germanium differs from silicon, titanium, zirconium, and thorium in that it can be prepared from the dioxide by reduction with carbon at a red heat, thus showing some approach to the ready reduction of the oxides of tin and lead.

Germanium tetrachloride, $GeCl_4$ (boiling-point 86°), **germanium chloroform,** $GeHCl_3$ (boiling-point 72°), and **germanium oxychloride,** $GeOCl_2$ (*boiling-point* much above 100°), are liquids which resemble not only the corresponding silicon-compounds, but also the carbon-compounds CCl_4, $CHCl_3$, and $COCl_2$. The **tetrafluoride,** $GeF_4,3H_2O$, can be prepared by the action of hydrofluoric acid on the dioxide. **Potassium germanifluoride,** K_2GeF_6, is isomorphous with the silicifluoride, $(NH_4)_2SiF_6$.

The **monoxide,** GeO, and **monosulphide,** GeS, are the principal examples of bivalent compounds of germanium.

50. TIN. Sn = 119·0.

Occurrence.

Tin has been found occasionally in the native state, but the principal ore is the **dioxide,** SnO_2. This has been mined from very early times as CASSITERITE or TINSTONE, *e.g.*, in Cornwall, where it occurs in mineral veins associated with tungsten (p. 747) and with arsenical copper pyrites; it is also found as STREAM TIN in the gravel or sand formed by the disintegration of rocks containing these veins. Cassiterite is sometimes associated in mineral-veins with fluoriferous minerals, such as topaz,

mica, apatite, and fluor; it is then thought to be of pneumolytic origin (p. 299), *e.g.*, formed by the hydrolysis of the gaseous chloride or fluoride. Less frequently TIN PYRITES (SnS, mixed with sulphides of copper, iron, and zinc) is found. In modern times, important deposits of tin have been discovered in the East Indies, *e.g.*, in the Malay States and particularly in the island of Banca.

Smelting of Tin.

The smelting of tin depends on the simple reduction shown in the equation

$$SnO_2 + C = Sn + CO_2.$$

The ore is roasted to remove sulphur and arsenic, and if necessary is roasted with soda-ash and extracted with water to free it from the more acid oxide of tungsten. The mineral is then mixed with anthracite and smelted in a reverberatory furnace (Fig. 248, p. 690), from which the metal is drawn off into moulds. The crude tin is purified by LIQUATION, a process in which the pure metal is run off and separated from the less fusible impurities by cautious heating.

Properties of Tin.

(*a*) *Allotropy.*—Tin is a white lustrous metal which melts at 232°. Like iron, it is trimorphous, with an upper transition temperature at 161° and a lower transition temperature at 18°. Below 18° the ordinary **white tin** of density 7·28 is liable to pass into **grey tin** of density 5·7, the change being accompanied by expansion and disintegration of the metal. At ordinary temperatures the change is very slow, and may not set in for many centuries; but it is stimulated by inoculation with grey tin and is accelerated very considerably by cooling, *e.g.*, to − 50°. Several cases are on record in which ingots of tin, tin buttons, organ pipes, medals, pewter pots, etc., have undergone this change during severe winters. The reverse change, which is accompanied by a

FIG. 244.—TIN PLAGUE.
The conversion to grey tin is still incomplete after more than two centuries.

marked contraction of the metal, takes place rapidly when hot water is poured over grey tin.

The conversion of white tin into grey tin takes place most readily where nuclei of grey tin are already present; the change therefore spreads by infection and is commonly known as TIN PLAGUE (Fig. 244: compare the conversion of prismatic into rhombic sulphur, Fig. 132, p. 320). On account of the slowness of the allotropic change, the transition temperature was determined by an electrical method; a cell was constructed (Fig. 245) with ammonium stannic chloride, $2NH_4Cl,SnCl_4$, as the electrolyte and white and grey tin at the electrodes. The electromotive force of this cell was found to vanish at 18°, showing that both forms of the metal were equally stable at this temperature; below 18°, a current flowed through the solution from white

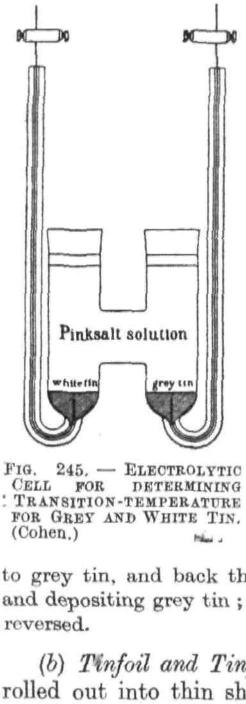


FIG. 245. — ELECTROLYTIC CELL FOR DETERMINING TRANSITION-TEMPERATURE FOR GREY AND WHITE TIN. (Cohen.)

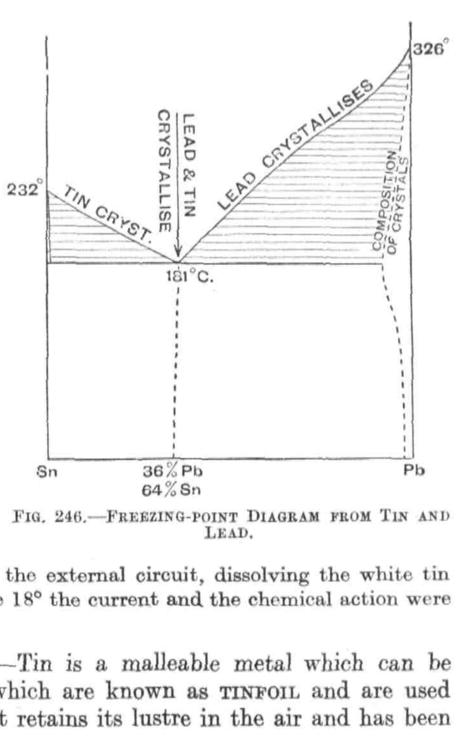


FIG. 246.—FREEZING-POINT DIAGRAM FROM TIN AND LEAD.

to grey tin, and back through the external circuit, dissolving the white tin and depositing grey tin; above 18° the current and the chemical action were reversed.

(*b*) *Tinfoil and Tinplate*.—Tin is a malleable metal which can be rolled out into thin sheets which are known as TINFOIL and are used extensively for wrapping. It retains its lustre in the air and has been used occasionally for casting medallions, etc. On account of its resistance to corrosion it has been used from very early times for lining or TINNING copper vessels by pouring into them a small quantity of molten tin. The "tins" used for packing biscuits, etc., consist of TINNED-PLATE made by dipping thin sheet steel, after cleaning or pickling it with acid, into baths of molten tin; the surface thus produced is brighter and cleaner than that of galvanised iron. Unlike zinc, the tin

has no protective action unless the surface of the iron is covered completely, and "tins" which have been scratched rust far more quickly than galvanised iron.

(c) *Alloys of Tin.*—The use of tin for hardening copper has been known from the beginning of the Bronze Age; the BRONZES formed by alloying together these two metals are described under copper (p. 834). Tin is also used with lead as a constituent of SOLDER; the melting-point of the metal is lowered from 232° to a minimum of 181° in the alloy containing 36 per cent. of lead (Fig. 246); this eutectic mixture (Fig. 247) is known as FINE SOLDER. An alloy of equal parts of tin and lead which begins to solidify at 220° is known as COMMON SOLDER, whilst an alloy of two parts of lead and one part of tin which begins to solidify at 260° is known as PLUMBER'S SOLDER, or COARSE SOLDER. PEWTER is a mixture of tin and lead containing about 80 per cent. (or more) of tin. TIN AMALGAM is used for coating glass mirrors; the amalgam is prepared by the addition of mercury to a sheet of tinfoil, which is pressed against the surface of the glass so as to squeeze out the excess of mercury.

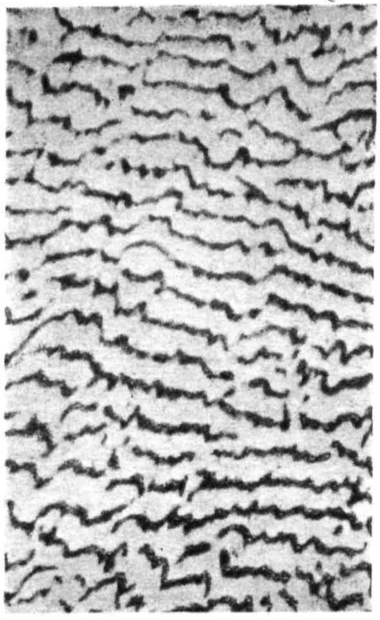


FIG. 247.—EUTECTIC ALLOY OF TIN AND LEAD.
(White = tin, black = lead.) Notice the predominance of tin in the eutectic alloy.

Fusible Alloys and Solders.

Of the common metals which are solid at atmospheric temperatures and fairly permanent in air, the most readily fusible are:

	M.-pt.		*M.-pt.*		*M.-pt.*
Antimony	.. 630°	Lead ..	.. 327°	Bismuth	.. 271°
Zinc ..	.. 419°	Cadmium	.. 321°	Tin ..	.. 232°

The last four metals, which melt within a range of less than 100° from one another, will mix in all proportions in the liquid state, but have only a very restricted power of forming solid solutions with one

another,* and do not yield intermetallic compounds. They therefore give rise to eutectic alloys which melt even more readily than the pure metals, *e.g.*,

Pb + Cd, 249°	Cd + Sn, 177°	Bi + Sn, 136°
Pb + Sn, 181°	Cd + Bi, 146°	Bi + Pb, 120°

The ternary eutectics melt at temperatures down to about 90° and the quaternary eutectic of these four metals melts at about 60°.

The binary eutectic of lead and tin has been described above as soft solder; the ternary eutectic of lead, tin, and bismuth, or an approximation to it, is described below (p. 715) as Rose's alloy, whilst Wood's alloy (p. 715) approximates to the quaternary alloy of lead, tin, bismuth, and cadmium. The binary eutectic of lead and antimony, which melts at 246°, is used in casting type (*e.g.*, in linotype machines, p. 709) in preference to the more fusible alloys described above, in part because of the hardness which the antimony imparts to the alloy, but mainly because of the unique property of expanding on solidification which this metal possesses. Tin is also hardened by antimony in solid solution or as SnSb (p. 710).

It is obvious that metals of low melting-point, mixed together in such proportions as to give binary, ternary, or quaternary eutectics, are ideal materials for making fusible alloys; and even cast iron owes its fusibility to the fact that iron and carbon form an eutectic alloy. Similar considerations govern the choice of metals for use as solders. These should resemble the metal which is to be soldered as closely as possible in everything but fusibility, and this points at once to the use of an alloy with some second metal which forms an eutectic with the first, as in the solder of lead and tin used in plumbing. In other cases, however, solid solutions of low melting-point may be used; thus gold is usually soldered with an alloy of gold and copper, which form a complete series of solid solutions, but with a deep minimum in the freezing-point curve; silver may be added to this alloy to maintain a suitable standard of value, but its effect on the melting-point of the solder is not important; if greater fusibility is required, zinc is added, *e.g.*, by using brass in place of copper in preparing the solder. Again copper goods are frequently "brazed," *i.e.*, soldered with brass; this is a solid solution of copper and zinc, but since copper melts at 1083° and zinc at 419°, and the melting-point curve does not diverge in any extreme way from a straight line, the melting-point of the copper can be lowered to any desired extent (but not below 419°) by alloying it with zinc.

* Lead will take up 10 per cent. of bismuth, 8 per cent. of tin, or 4 per cent. of cadmium in solid solution. Tin will take up 8 per cent. of cadmium, 6 per cent. of bismuth, or 1 per cent. of lead. Bismuth will take up 10 per cent. of lead, but not tin or cadmium. Cadmium will take up tin, but not lead or bismuth.

Chemical Properties of Tin.

(*a*) *Valency.*—Tin forms two series of compounds, namely, STANNOUS COMPOUNDS, in which the metal is bivalent, and STANNIC COMPOUNDS, in which it is quadrivalent. The lower oxide, SnO, is a base which dissolves readily in acids to form stannous salts, *e.g.*,

$$SnO + 2HCl = SnCl_2 + H_2O,$$

but it must be classed amongst the amphoteric oxides (p. 529), since it also dissolves in alkalies to form stannites, which are said to be analogous to the formates,

$$Sn(OH)_2 + NaOH = \underset{\text{Sodium stannate}}{H{\cdot}SnO{\cdot}ONa} + H_2O,$$

compare

$$CO + NaOH = \underset{\text{Sodium formate}}{H{\cdot}CO{\cdot}ONa}.$$

The higher oxide, SnO_2, is also amphoteric, since it gives stannic salts with acids and stannates with bases, *e.g.*,

$$SnO_2 + 4HCl = \underset{\text{Stannic chloride}}{SnCl_4} + 2H_2O.$$

$$SnO_2 + 2NaOH = \underset{\text{Sodium stannate}}{Na_2SnO_3} + H_2O.$$

(*b*) *Oxidation and Chlorination.*—Tin does not combine directly with nitrogen or carbon, and, like lead (p. 692) and bismuth (p. 715), gives only minute traces of a hydride, presumably SnH_4, when reduced with hydrogen. When heated in air or oxygen it is readily converted into the white **stannic oxide**, SnO_2; the first suggestion of the part played by the atmosphere in combustion is found in a memoir by Jean Rey, (1630), "On an enquiry into the cause wherefore tin and lead increase in weight on calcination." When heated in a limited quantity of air (p. 61) grey **stannous oxide,** SnO, is formed.

Tin combines directly with chlorine to form **stannic chloride,** $SnCl_4$, and displaces hydrogen from hydrogen chloride gas to form **stannous chloride,** $SnCl_2$. It dissolves in hydrochloric acid to form stannous chloride and hydrogen,

$$Sn + 2HCl = SnCl_2 + H_2.$$

It also dissolves in dilute nitric acid, but stannic nitrate, $Sn(NO_3)_4$, is not stable and decomposes into an insoluble hydrated stannic oxide.

Stannous Compounds.

Stannous chloride, $SnCl_2$, is prepared by dissolving tin in hydrochloric acid. It separates from solution as the **dihydrate,** $SnCl_2,2H_2O$, which is known as TIN-SALT. It dissolves in less than its own weight of water, but, unless some additional hydrochloric acid is added, a basic chloride is deposited on dilution. Like zinc chloride (p. 872), the hydrated salt can, however, be dried in a vacuum without losing hydrochloric acid.

The anhydrous salt, which is most readily prepared from metallic tin by heating it in a current of hydrogen chloride or with mercuric chloride, melts at 247° and boils at 603°.

Stannous chloride is a powerful reducing agent; it will convert mercuric chloride into mercurous chloride or into mercury,

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2,$$
$$SnCl_2 + HgCl_2 = SnCl_4 + Hg,$$

and ferric chloride into ferrous chloride,

$$SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2.$$

In presence of an excess of hydrochloric acid the reduction of the ferric salt proceeds rapidly, and the disappearance of the yellow colour of the ferric salt is almost sharp enough to be made the basis of a method of titration; actually, however, the titration is carried out by using an excess of stannous chloride to reduce the ferric salt, removing the excess by the addition of mercuric chloride, and then oxidising the ferrous salt back again to the ferric state with a standard solution of potassium dichromate.

Stannous oxide, SnO, is obtained as a grey powder when tin is heated with a limited volume of air. **Stannous hydroxide,** $Sn(OH)_2$, is formed by the addition of sodium hydroxide to a solution of stannous chloride, but dissolves in an excess of alkali, forming **sodium stannite,** $NaHSnO_2$:

$$Sn(OH)_2 + NaOH = NaHSnO_2 + H_2O.$$

The alkaline solution is a powerful reducing agent and was used by Stas (p. 98) in preparing carbonic oxide free from carbon dioxide and oxygen.

Stannous sulphide, SnS, can be prepared by direct combination of tin and sulphur. It is obtained as a brown precipitate by the action of sulphuretted hydrogen on a solution of stannous chloride:

$$SnCl_2 + H_2S = SnS + 2HCl.$$

Yellow ammonium sulphide converts it into stannic sulphide and thence into a soluble **ammonium thiostannate,**

$$SnS + Am_2S_2 = Am_2SnS_3.$$

Stannous sulphate, $SnSO_4$, is a soluble salt obtained by dissolving tin in dilute sulphuric acid, and **stannous nitrate,** $Sn(NO_3)_2$, is formed when tin is dissolved in very dilute nitric acid.

Stannic Compounds.

Stannic chloride, $SnCl_4$, is prepared by the action of chlorine on metallic tin,

$$Sn + 2Cl_2 = SnCl_4;$$

the action is accompanied by liberation of heat, so that the iron vessel in which the action is carried out must be cooled externally with water.

The product is a liquid which boils at 114°, freezes at − 33°, and fumes strongly in moist air ; on account of this last property, stannic chloride has been used to produce visible smoke in gas-shells. Although resembling the non-metallic chlorides, *e.g.*, CCl_4, in some of its properties, it dissolves in water without marked decomposition and separates from solution as a crystalline salt with $8H_2O$, $5H_2O$, $4H_2O$, or $3H_3O$, according to the temperature. Above 83°, two liquid layers may be formed, an upper layer consisting mainly of water and a lower layer consisting mainly of fused stannic chloride. From dilute solutions stannic hydroxide is deposited. Stannic chloride also combines with ammonia to form the compound $SnCl_4,4NH_3$, which dissolves in water without decomposition, and with a number of non-metallic chlorides, oxychlorides, etc., *e.g.*, with $2SCl_4$, N_2O_3, $2NOCl$, $4NOCl$, PCl_5, and $POCl_3$.

Stannic chloride is used extensively in dyeing, either as the **pentahydrate,** $SnCl_4,5H_2O$, or as **ammonium stannichloride** or PINK SALT, $2NH_4Cl,SnCl_4$ or $(NH_4)_2SnCl_6$; its use as a mordant (p. 662) depends on the ready deposition of stannic hydroxide from weak solutions of the chloride.

Stannic oxide, or **tin dioxide**, SnO_2, occurs naturally as TINSTONE or CASSITERITE and is the principal ore of tin. It is isomorphous with zircon, $ZrSiO_4$, and it has therefore been suggested that it is really a stannic stannate, $SnSnO_4$. The dioxide can be prepared artificially by burning the metal in air, or by oxidising it with nitric acid and igniting the residue.

When fused with caustic alkalies, stannic oxide is converted into soluble STANNATES, *e.g*, **sodium stannate,** Na_2SnO_3, and **potassium stannate,** K_2SnO_3. These two salts both crystallise from water with $3H_2O$, and are probably hydroxides of the type $Na_2Sn(OH)_6$ and $K_2Sn(OH)_6$, compare $K_2Pt(OH)_6$ and K_2PtCl_6 (p. 817). On the addition of acid to solutions of these compounds, **stannic acid,** H_2SnO_3, is precipitated.

An insoluble **metastannic acid** is formed when tin is acted on by nitric acid ; it appears to have the same composition as stannic acid, but forms a series of salts which are distinct both in their composition and in their properties from the soluble stannates referred to above.

Stannic sulphide, SnS_2, is a golden-yellow compound which has long been prepared as a pigment, under the name of MOSAIC GOLD, by heating tin with sulphur in presence of sal-ammoniac and mercury. It is also formed as a yellow precipitate by the action of sulphuretted hydrogen on a soluble stannic salt. The precipitate dissolves readily in alkaline sulphides forming soluble THIOSTANNATES, *e.g.*, **potassium thiostannate,** $K_2SnS_3,3H_2O$.

Stannic sulphate, $Sn(SO_4)_2$, and **stannic nitrate**, $Sn(NO_3)_4$, have been prepared in presence of the strong acids, but are rapidly decomposed by water (compare lead).

Detection and Estimation of Tin.

Compounds of tin when heated on charcoal are readily reduced, giving a malleable white bead of the metal. Metallic tin can also be precipitated from solution by the addition of metallic zinc.

Soluble stannous salts give a brown precipitate of **stannous sulphide,** SnS, with sulphuretted hydrogen ; this is insoluble in dilute acids, but dissolves in yellow ammonium sulphide. On the addition of ammonia or caustic alkali, stannous salts give a white precipitate of **stannous hydroxide,** $Sn(OH)_2$, but the precipitate is soluble in an excess of the caustic alkali. Stannous salts can also be detected by their reducing action ; thus, stannous chloride reduces ferric chloride to ferrous chloride, and when added to a solution of mercuric chloride, yields first a white precipitate of calomel and then a grey precipitate of mercury.

Stannic salts give with sulphuretted hydrogen a yellow precipitate of **stannic sulphide,** SnS_2, which dissolves in ammonium sulphide, but not in ammonium carbonate (difference from arsenic sulphide). Caustic alkalies precipitate **stannic hydroxide,** $Sn(OH)_4$, which dissolves readily in an excess of the reagent.

The quantitative estimation of tin depends on conversion into the **dioxide,** SnO_2. This can often be obtained by the direct action of nitric acid upon alloys of tin, such as copper coinage, which contains 4 per cent. of this metal and leaves an insoluble residue of metastannic acid when the copper and zinc are dissolved in nitric acid. From solution, the tin can be precipitated as a hydroxide by means of ammonia, or as a sulphide by means of sulphuretted hydrogen, the product being converted into the dioxide by heating in air.

The atomic weight of tin rests mainly on exact determinations of the ratios $K_2SnCl_6 : Sn$, $(NH_4)_2SnCl_6 : Sn$, and $SnBr_4 : Sn$, the tin being deposited electrolytically from a solution of the bromide.

82. LEAD. Pb = 207·20.

Occurrence.

Native lead has been found occasionally. The principal ore is **lead sulphide** or GALENA, PbS ; this is found in large quantities in mineral veins, in which it is associated with calcite, quartz, fluorspar, or barytes. Very frequently galena and blende are associated together in the vein. Lead has been mined since the Roman period in Derbyshire and Shropshire, as well as in Spain. More recently very large deposits have been worked at Broken Hill in Australia. Less common ores of lead, which are believed to have been formed from galena by secondary changes, include **lead carbonate** or CERUSSITE, $PbCO_3$, isomorphous with aragonite, $CaCO_3$, and with witherite, $BaCO_3$, and **lead sulphate** or ANGLESITE, $PbSO_4$, isomorphous with barytes, $BaSO_4$.

Smelting of Lead.

The traditional method of smelting galena depends on partial oxidation in a reverberatory furnace,

$$2PbS + 3O_2 = 2PbO + 2SO_2,$$
$$PbS + 2O_2 = PbSO_4;$$

further heating in the absence of air then causes the separation of metallic lead,

$$2PbO + PbS = 3Pb + SO_2,$$
$$PbSO_4 + PbS = 2Pb + 2SO_2.$$

The REVERBERATORY FURNACE (Fig. 248) is used extensively in metallurgical and chemical operations, when it is desired to heat a material without

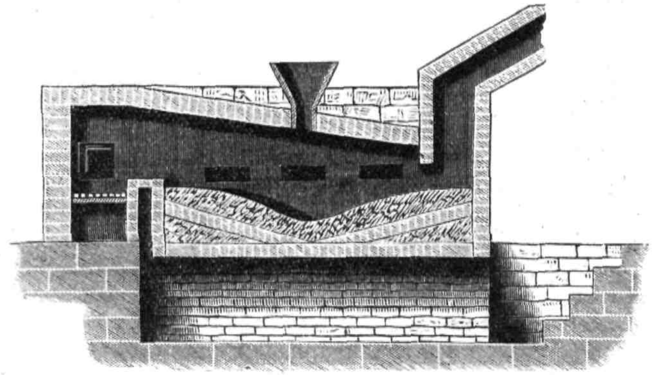


FIG. 248.—REVERBERATORY FURNACE.

mixing it with the fuel; the chief feature of the furnace is the throwing down upon the bed of the furnace of heat radiated from the roof, on which the flames from the fire impinge. The smelting of lead is, however, now carried out usually in small blast-furnaces.

Ores which contain silica and which yield lead silicate on roasting are reduced by carbon in the presence of lime,

$$2PbSiO_3 + 2CaO + C = 2CaSiO_3 + CO_2 + 2Pb.$$

Ores which contain copper are reduced most conveniently by the use of metallic iron,

$$PbS + Fe = FeS + Pb.$$

The crude lead may contain silver, arsenic, antimony, bismuth, copper, iron, and zinc; these render the metal hard. All these impurities except bismuth, copper, and silver are more easily oxidised than lead and can be burnt out by heating the metal in a furnace; copper forms with lead a compound or alloy of high melting-point which separates in the scum; bismuth is eliminated with silver in the Pattinson process of desilvering (p. 691).

Desilvering of Lead.

Lead which contains not less than 2 ounces of silver to the ton can be worked profitably for silver. Two principal methods of separation are employed, each depending on a simple physico-chemical law.

(*a*) *Pattinson's process* depends on the fact that when crude lead begins to solidify the crystals which separate consist of pure lead. By removing these the liquid metal is enriched in silver. If these crystals could be drained completely, a single operation would suffice to free them from silver; actually so much liquid is carried with them that the crystallisation must be repeated several times in a series of pots in order to produce pure lead on the one hand and a concentrated silver alloy on the other.

(*b*) *Parkes' process* depends on the fact that silver can be extracted from lead by the addition of zinc. These two metals float one upon the other, the composition of the two layers being as follows:

Upper layer . . .	Zn =	98·86	Pb =	1·14%
Lower layer . . .	Pb =	98·70	Zn =	1·30%

Any silver which may be present distributes itself in a fixed ratio between these, the concentration of silver in the upper layer being 40 times as great as in the lower layer. Thus, if a ton of lead were stirred up with half a hundredweight of zinc the zinc would take up about half of the silver from the lead. In practice lead can be desilvered by using only 1 per cent. of zinc, since when only a small proportion of zinc is used compounds of silver and zinc, *e.g.*, AgZn, which melt at a higher temperature than zinc itself, crystallise out and can be skimmed off and drained in a perforated ladle. The zinc in the skimmings is removed by distillation as metal, or as chloride, after which the lead is removed by cupellation, leaving behind a button of pure silver. The zinc remaining in the desilvered lead can be removed by oxidation with steam, and sold as " zinc white "; this method may also be applied to the treatment of the zinc-skimmings which carry the silver.

Physical Properties of Lead.

Lead is a heavy metal of density 11·34. It is very soft and is so plastic that it can be squirted under pressure into the form of rods or pipes; it can also be rolled into sheets which are used for roofing, and for lining vats, etc., in chemical plant, or into foil which is used for packing tea. The freshly cut surface of lead possesses a bright lustre, although the metal is much darker than silver or tin, and the clean metal can be cold-welded like gold, but the surface soon tarnishes and becomes dull on exposure to air. Lead melts at 327°, and the eutectic alloy of lead and tin at 181°; mixtures of lead and tin are therefore used as solders (p. 684). Alloys of lead, tin, and bismuth, with or without cadmium, are used as fusible alloys (p. 715). Lead used for making lead shot is hardened by the addition of arsenic, whilst type metal

consists of lead hardened by means of antimony; lead may also be hardened by the addition of calcium.

Chemical Properties of Lead.

Although lead is a base metal, it shows some points of resemblance to silver. Thus the two metals are constantly associated together in the sulphides PbS and Ag_2S, which are isomorphous. Silver and lead are also remarkable for forming insoluble salts, such as lead sulphate and silver chloride, which are made use of in analysis. Lead can be deposited from solutions of its salts by electrolysis; the nitrate gives a loose crystalline deposit, but the metal can be deposited in a coherent form from solutions of lead silicifluoride, $PbSiF_6$ (just as silver can be electrodeposited from potassium argenticyanide, $KAgC_2N_2$), and this salt has been used as an electrolye in the electrolytic refining of lead. Lead can also be precipitated from solution by metals which are more readily oxidised, as in the formation of a LEAD TREE by suspending a piece of zinc in an aqueous solution of lead nitrate or lead acetate; this experiment resembles the precipitation of metallic silver from silver nitrate by means of copper,

$$Zn + Pb(NO_3)_2 = Pb + Zn(NO_3)_2,$$

compare $$Cu + 2AgNO_3 = 2Ag + Cu(NO_3)_2.$$

When heated in a current of air, metallic lead burns to the **monoxide,** litharge, PbO; further roasting in the air converts this into red lead. Lead also combines directly with chlorine to form the **chloride,** $PbCl_2$, and with sulphur to form the **sulphide,** PbS. It does not combine directly with carbon or nitrogen, but a highly explosive compound of lead and nitrogen, **lead azide,** PbN_6, can be prepared by indirect methods (p. 385) and has been used in making detonators. Like tin and bismuth (p. 715) it gives minute traces of a **hydride,** presumably PbH_4, when reduced; the property of forming hydrides is therefore possessed by the last four members of each of the periods II to V.

Lead is not attacked by pure water in the absence of air, but water containing carbon dioxide dissolves considerable quantities of lead, probably in the form of the **bicarbonate,** $Pb(CO_3H)_2$; this action is, however, checked by the presence of mineral carbonates or sulphates, so that hard water can be carried in lead pipes without giving rise to lead-poisoning. In certain instances very soft moorland waters, containing carbon dioxide but no mineral salts, have been hardened by the introduction of small quantities of lime, in order to remove the risk of lead-poisoning from the lead pipes of the domestic water supply.

Like copper, lead is not readily attacked by dilute acids in the absence of air, but when air is present it is rapidly corroded even by such weak acids as acetic acid and carbonic acid. It dissolves readily in dilute nitric acid, oxides of nitrogen being liberated instead of hydrogen; concentrated sulphuric acid also dissolves it to an appreciable

extent in spite of the sparing solubility of the sulphate in water. Like silver, lead is said to be attacked also by concentrated hydrochloric acid, hydrogen being liberated and lead chloride formed.

Lead forms two series of salts, namely, PLUMBOUS SALTS, in which the metal is bivalent, and PLUMBIC SALTS, in which the metal is quadrivalent; the plumbic salts are, however, difficult to prepare and are readily decomposed by water.

Lead and Oxygen.

Lead monoxide, PbO, derives its name of LITHARGE (λίθος, a stone, ἄργυρος, silver) from the fact that it is obtained as a stony mass when lead is burnt to recover the silver from it. It is a very heavy yellow or brown compound of density 9·4 and melts at about 900°.

Lead monoxide is a base which imparts a blue colour to litmus and combines readily with acids.

Plumbous hydroxide, $Pb(OH)_2$, is formed by the action of air and water on lead in the absence of carbon dioxide and can be prepared by precipitation of a soluble plumbous salt by an alkali. It is soluble in strong caustic alkalies and crystallises out when these become carbonated (compare alumina). Plumbous hydroxide is, however, essentially a base, *since it turns litmus blue, absorbs carbon dioxide from the* air, and dissolves readily in acids.

Red lead or **minium**, Pb_3O_4 (?), is obtained by roasting litharge gently in the air. The red compound is generally formulated as Pb_3O_4, but commercial samples vary in composition, containing only enough oxygen to correspond with the presence of 44 to 92 per cent. of a compound of this formula. A product of the composition Pb_3O_4 can, however, be prepared (i) by roasting lead carbonate, (ii) by precipitating together alkaline solutions of the monoxide and dioxide and gently heating the product, or (iii) by heating together a mixture of $2PbO + PbO_2$. The excess of lead monoxide in commercial red lead can be extracted by an alkali, by acetic acid, an alkaline acetate or acetate of lead, without destroying its red colour; towards strong acids, however, red lead behaves like a mixture of PbO and PbO_2 and yields a plumbous salt and lead peroxide. It is decomposed by heating, and if heated in hydrogen will take fire and burn, leaving a residue of metallic lead.

Plumbic oxide or **lead peroxide**, PbO_2, is prepared most readily by extracting red lead with nitric acid, when the red colour disappears, giving a colourless solution of plumbous nitrate and leaving a brown residue of the peroxide. It is produced by the action of many oxidising agents on litharge or on plumbous salts, and is precipitated at the anode when lead nitrate is electrolysed between platinum electrodes,

$$Pb(NO_3)_2 + 2\mathit{NO}_3 = Pb(NO_3)_4$$
$$Pb(NO_3)_4 + 2H_2O = PbO_2 + 4HNO_3;$$

this action is used in the quantitative estimation of lead. Lead

peroxide is stable up to 300°, but decomposes at higher temperatures into litharge and oxygen. It combines with sulphur dioxide to form lead sulphate, and oxidises many organic compounds, including oxalic acid,

$$PbO_2 + 2HNO_3 + H_2C_2O_4 = Pb(NO_3)_2 + 2H_2O + 2CO_2;$$

oxalic acid is therefore used to estimate lead peroxide, and indirectly to estimate the "available oxygen" in red lead. For this purpose the red lead is dissolved in a mixture of nitric acid and an excess of a standard solution of oxalic acid; the excess of oxalic acid, which has not been oxidised by the lead oxide, is then estimated by oxidation with potassium permanganate.

Lead peroxide is amphoteric, since it yields unstable plumbic salts when acted upon by acids, and plumbates when acted on by alkalies. Thus, cold concentrated hydrochloric acid gives plumbic chloride,

$$PbO_2 + 4HCl \rightleftharpoons PbCl_4 + 2H_2O;$$

strong hydrobromic acid also gives solutions from which plumbic salts such as $PbBr_4,2KBr$ or K_2PbBr_6 can be precipitated, although in presence of water they are decomposed and lead peroxide is thrown down again; and the double salt, $PbF_4,3KF,HF$, from which plumbic fluoride is prepared, is obtained by the action of potassium hydrogen fluoride and hydrogen fluoride on lead peroxide. On the other hand, by the action of alkalies on lead peroxide, ORTHOPLUMBATES, derived from the acid H_4PbO_4, and METAPLUMBATES, derived from the acid H_2PbO_3, can be prepared. Thus, the characteristic constituent of red lead to which the formula Pb_3O_4 has been given can be regarded as an orthoplumbate, $Pb_2(PbO_4)$, whilst the **sesquioxide**, Pb_2O_3, which is obtained as a yellow precipitate by the action of sodium hypochlorite on soluble plumbous salts, may be regarded as a metaplumbate, $Pb(PbO_3)$.

Soluble Plumbous Salts.

Plumbous fluoride, PbF_2, like calcium fluoride, is almost insoluble in water, but **lead silicifluoride**, $PbSiF_6$, is soluble and has been used as the electrolyte in the electrolytic refining of lead.

Plumbous chloride, $PbCl_2$, can be formed by direct combination of lead with chlorine, by boiling the oxides with hydrochloric acid, or by precipitation from a soluble salt of lead by the addition of hydrochloric acid, or of a soluble chloride. It dissolves in hot water and crystallises out in needles on cooling; water dissolves 3 per cent. of the salt at 100° and 1 per cent. at 20°. It melts at 500° and boils below 1000°, the density of the vapour corresponding with the formula $PbCl_2$. Lead chloride forms complete series of solid solutions with $SrCl_2$ and $SnCl_2$, but gives an eutectic with PbI_2, and forms compounds such as PbFCl (compare CaFCl, Fig. 229, p. 624) with PbF_2.

Plumbous iodide, PbI_2, crystallises from hot water in brilliant golden scales; its solubility diminishes from 0·4 per cent. at 100° to 0·06 per cent. at 20°.

Plumbous chlorate, $Pb(ClO_3)_2$, and **plumbous perchlorate**, $Pb(ClO_4)_2$, like the corresponding salts of silver, are freely soluble in water.

Lead nitrate, the most important of the soluble salts of lead, is prepared by the action of nitric acid on lead, or on the oxide or carbonate. It crystallises without water of crystallisation and decomposes when heated, giving litharge, nitrogen peroxide, and oxygen.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

It forms an explosive mixture with sulphur and is a constituent of some commercial and military explosives, where its high density, 4·4, gives it an advantage over ammonium nitrate and sodium nitrate.

Lead acetate, $Pb(C_2H_3O_2)_2,3H_2O$, prepared by the action of acetic acid on litharge, is an important soluble salt of lead. It has a sweet taste and is therefore known as SUGAR OF LEAD, but like all the soluble salts of lead it is poisonous. It is used extensively in medicine and in dyeing. It dissolves litharge, giving the solution known as BASIC LEAD ACETATE, which is used as a reagent in organic chemistry, and probably contains the **basic acetate**, $HO{\cdot}Pb{\cdot}C_2H_3O_2,Pb(C_2H_3O_2)_2$.

Plumbous Sulphide, Sulphate, and Chromate.

Plumbous sulphide, PbS, the principal ore of lead, is found as GALENA in mineral veins, sometimes in cubic crystals which may attain considerable size (Fig. 249). It can be prepared by the direct combination of lead and sulphur or by the action of sulphuretted hydrogen on the oxides or salts of lead. The mineral is of high density, 7·7, and can therefore be separated from rock and from lighter minerals such as blende by washing with water. It melts at about 1100° and can be vaporised in the absence of air. When heated in air or oxygen it is converted into the oxide, PbO, or the sulphate, $PbSO_4$, whilst chlorine converts it into plumbous chloride, $PbCl_2$, with liberation of sulphur.

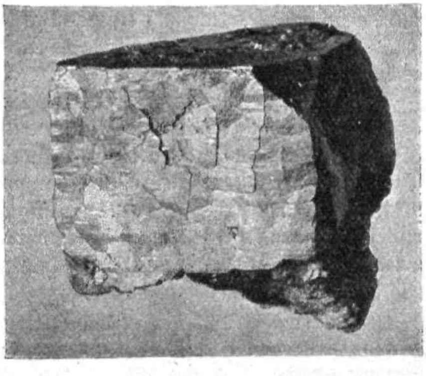


FIG. 249.—LARGE CUBE OF GALENA.
The triangular faces on the top corners are parts of an octahedron.

Plumbous sulphate, $PbSO_4$, occurs as the mineral ANGLESITE, in transparent, colourless, orthorhombic crystals, isomorphous with

barytes, $BaSO_4$. It can also be prepared by precipitation from a soluble salt of lead by sulphuric acid or a sulphate. It is a heavy compound, which is very sparingly soluble in water (1 part in 30,000) and even less soluble in presence of alcohol; on account of its granular character, lead sulphate is used not only for the estimation of lead but also in place of barium sulphate for the estimation of sulphuric acid. It is appreciably soluble in concentrated sulphuric acid and is precipitated on dilution; it also dissolves in solutions of various salts such as sodium acetate and ammonium nitrate. By very strong heating it is converted into litharge. A number of **basic sulphates** are also known, *e.g.*, $PbSO_4,PbO$ (m.p. 965°), $PbSO_4,2PbO$ (m.p. 948°) and $PbSO_4,3PbO$ crystallise out from solutions of lead sulphate in molten litharge.

Plumbous chromate, $PbCrO_4$, occurs naturally as the mineral CROCOITE, and is obtained as a yellow precipitate of CHROME YELLOW by the action of potassium chromate or dichromate on a solution of lead acetate or nitrate. It melts to a reddish-brown mass which is used as an oxidising agent in the combustion of organic compounds containing halogens. When boiled with a dilute alkali it is converted into a **basic chromate**, $PbCrO_4,PbO$, known as CHROME RED, which is used extensively as a pigment. A second **basic chromate** with the formula $2PbCrO_4,PbO$, also red in colour, occurs as a mineral and has been prepared artificially.

Plumbous Carbonates and Silicates.

Plumbous carbonate, $PbCO_3$, is found in a crystalline form as CERUSSITE, a mineral which is isomorphous with aragonite, $CaCO_3$. It can be prepared artificially by passing carbon dioxide into a solution of lead acetate. When heated it loses carbon dioxide and leaves a residue of litharge.

When a soluble salt of lead is precipitated by means of an alkaline carbonate, basic carbonates are formed, probably by the decomposition of a double carbonate (compare magnesium, p. 618, and copper, p. 842). Two **basic carbonates** of definite composition, namely $PbCO_3,Pb(OH)_2$ and $2PbCO_3,Pb(OH)_2$, have been found as minerals. WHITE LEAD, which has been prepared as a pigment from very early times by the action of carbon dioxide and air upon metallic lead, consists mainly of the second of these compounds.

In the DUTCH PROCESS of manufacture, rolls of sheet lead are exposed in pots over acetic acid and are acted on by the vapours from spent tannery waste. The pigment prepared by this method has the advantage of very great covering power, and is the traditional basis for the majority of white and coloured paints; during the past 50 years it has been displaced in part by barytes, $BaSO_4$ (ground or precipitated, p. 647), by zinc white or by lithopone (p. 647), especially in France, where the use of lead paints has been prohibited on account of their poisonous properties. Many attempts have been made to prepare white lead by more rapid methods, *e.g.*, by

precipitation, but these usually give rise to a coarse product, the covering power of which is much inferior to white lead made by the old methods; some of the more recent processes have, however, achieved marked success in overcoming this fundamental difficulty.

Plumbous silicate, which is formed by the union of litharge with silica, *e.g.*,

$$PbO + SiO_2 = PbSiO_3,$$

is a constituent of lead glasses and is formed as a glaze on earthenware. The **orthosilicate,** Pb_2SiO_4, melts at 740°, and the **metasilicate,** $PbSiO_3$, melts at 770°. In order to diminish the risk of lead-poisoning, the litharge or white lead used for glazing may be "fritted" with silica and so converted into a silicate which is less readily soluble and therefore less dangerous than the oxide or carbonate.

Plumbic Salts.

Plumbic chloride, $PbCl_4$, can be prepared in solution by passing chlorine through plumbous chloride suspended in a concentrated solution of common salt. The double salt, **ammonium plumbichloride,** $PbCl_4,2NH_4Cl$ or $(NH_4)_2PbCl_6$, compare ammonium platinichloride, $(NH_4)_2PtCl_6$, can be prepared by saturating a solution of plumbous chloride in hydrochloric acid with chlorine and crystallising out the double salt by the addition of ammonium chloride; when the double salt is added to cold concentrated sulphuric acid, plumbic chloride separates as a yellow oil, of density 3·2, which solidifies when cooled to − 15°. Plumbic chloride decomposes into plumbous chloride and chlorine when heated and is decomposed by water, giving first an unstable hydrate and then lead peroxide and hydrochloric acid.

$$PbCl_4 = PbCl_2 + Cl_2$$
$$PbCl_4 + 2H_2O = PbO_2 + 4HCl.$$

Plumbic fluoride, PbF_4, has been separated by similar methods from the double salt, $PbF_4,3KF,HF$, prepared by the action of KHF_2 on PbO_2.

Plumbic sulphate, PbS_2O_8, which may also be regarded as a plumbous persulphate, is produced when strong sulphuric acid is electrolysed at a lead anode:

$$H_2SO_4 = 2H + SO_4; \quad Pb + 2SO_4 = PbS_2O_8.$$

Plumbic acetate or **lead tetracetate**, $Pb(C_2H_3O_2)_4$, prepared by the action of acetic acid on red lead, crystallises from the filtrate in colourless prisms and melts at 175°. As in the case of manganic acetate (p. 757), the acetate is exceptionally stable, perhaps on account of the inertness of this radical as compared with chlorine, or SO_4, etc.

The Lead Accumulator.

The lead accumulator (Fig. 250) consists of a series of *negative plates,* containing finely-divided lead supported on a lead grid, a series

of *positive plates* containing a paste of lead peroxide mounted in a lead grid, and an *electrolyte* consisting of pure sulphuric acid diluted with water to about 30 per cent. strength. The discharge of the cell may be represented by the equation

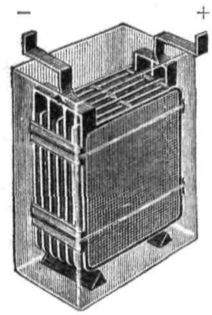


FIG. 250.—LEAD ACCUMULATOR.
The cell shown has four negative and three positive plates.

$$Pb + 2H_2SO_4 + PbO_2 = PbSO_4 + 2H_2O + PbSO_4,$$

and the charging of the cell by a reversal of this equation. The action is, however, probably more complex, and in particular the normal product of discharge cannot be a fully-formed crystalline lead sulphate, since this is not reduced and oxidised to Pb and PbO_2 on recharging the cell, but appears as white patches on the plate in cells in which SULPHATING has taken place. This formation of lead sulphate is most likely to occur when the cell is discharged, and the risk of sulphating is the principal factor which prevents the use of a higher concentration of sulphuric acid to increase the voltage and capacity of the cell.

Detection and Estimation of Lead.

Lead compounds when heated on charcoal in the blowpipe flame yield a malleable bead of metallic lead. From concentrated solutions of lead salts, hydrochloric acid precipitates the sparingly soluble **lead chloride,** $PbCl_2$, which can be recrystallised from hot water. Potassium chromate precipitates **lead chromate** or chrome yellow, $PbCrO_4$. From more dilute solutions lead can be precipitated in the form of **lead sulphate,** $PbSO_4$, by the addition of dilute sulphuric acid; but sulphuretted hydrogen, which precipitates the black **sulphide,** PbS, is a much more sensitive reagent, and is commonly used for detecting traces of lead, *e.g.*, in water for drinking.

Lead is estimated most readily in the form of the **sulphate,** by precipitation with dilute sulphuric acid in presence of alcohol; as the precipitate is granular and easily filtered, it is sometimes preferred to barium sulphate for the estimation of sulphates.

Lead can also be estimated electrolytically by depositing it as **lead peroxide** at the anode, from acid solutions which will not allow metallic lead to remain undissolved at the cathode.

The atomic weight of lead is based upon Stas's determinations of the ratios $Pb : Pb(NO_3)_2 : PbSO_4$. In more recent experiments the ratios $PbBr_2 : 2AgBr : 2Ag$ have been determined.

CHAPTER XXXVI

ARSENIC, ANTIMONY, AND BISMUTH

Atomic Number.	*Element.*	*Symbol.*	*Atomic Weight.*
7	Nitrogen	N	14·01
15	Phosphorus	P	31·04
33	Arsenic	As	74·96
51	Antimony	Sb	120·2
83	Bismuth	Bi	208·0

Classification.

The three elements *arsenic. antimony*, and *bismuth* are found on the ascending slopes of the long periods of Meyer's atomic volume curve and are therefore grouped with the two elements nitrogen and phosphorus, which occupy corresponding positions on the ascending slopes of the two short periods. The five elements,

7. *Nitrogen*, 15. *Phosphorus*, 33. *Arsenic*, 51. *Antimony*, 83. *Bismuth*,

immediately precede the elements of the oxygen and sulphur family,

8. *Oxygen*, 16. *Sulphur*, 34. *Selenium*, 52. *Tellurium*,

and the halogens,

9. *Fluorine*, 17. *Chlorine*, 35. *Bromine*, 53. *Iodine*;

but whilst the halogens are all non-metals, definite metallic properties appear in tellurium, the fourth member of the oxygen family, and a similar development of metallic properties can be recognised in arsenic, the third member of the nitrogen family.

In view of the fact that the first two members of the family are non-metals, whilst the last three are metals, the complete family of five elements covers a very wide range of properties, the gaps being specially wide between nitrogen and phosphorus and between phosphorus and arsenic. The three metallic elements, arsenic, antimony, and bismuth, are related together much more closely, since they occupy positions near the ends of the three long periods and form a natural group of closely-related elements, although they do not form a normal triad, since the interposition of the elements of the rare earths produces a wider separation between antimony and bismuth than between arsenic and antimony.

Physical Properties of the Group.

The physical properties of the members of this group are shown in the following table :

TABLE 78.—PROPERTIES OF THE ARSENIC GROUP.

	Density.	*Melting-point.*	*Boiling-point.*	*Specific Conductivity*† *at* 0°.
As .	5·72	817°*	616°‡	$2{\cdot}85 \times 10^4$
Sb .	6·62	630°	1440°	$2{\cdot}61 \times 10^4$
Bi .	9·80	271°	1420°	$0{\cdot}93 \times 10^4$
				Copper = $64{\cdot}0 \times 10^4$

* Under pressure. † In reciprocal ohms per cm. cube. ‡ Sublimation-point.

The three elements all possess the essential characteristics of metals ; indeed, arsenic and antimony, which have often been classified as non-metals, possess a higher electrical conductivity than bismuth, which has generally been admitted to be a metal. As in so many other cases, there is a marked increase of density with increasing atomic weight, and a progressive lowering of the melting-point similar to that which is noticed in mercury and cæsium, the heaviest elements of the families to which they belong, as well as the two most fusible metals ; the boiling-points, on the other hand, increase progressively from nitrogen to phosphorus, to arsenic, and finally to antimony and bismuth, which both boil a little above 1400°. The three elements are all coarsely crystalline and brittle, so that none of them can be drawn into wire or rolled into foil.

Chemical Properties of the Group.

The association of the two non-metals, nitrogen and phosphorus, with the three metals, arsenic, antimony, and bismuth, is justified by the tendency of all these elements to form tervalent and quinquevalent compounds, and by the isomorphism which links together the phosphates and the arsenates. As the atomic weight increases, however, the acidity of the oxides diminishes, and in the case of bismuth most of the derivatives contain this element as a base-forming constituent.

In its univalent compounds bismuth breaks away from arsenic and antimony and shows some similarity to gold ; thus, the monochloride, BiCl, resembles aurous chloride, AuCl, in that it breaks down when heated, probably as shown in the equation :

$$3BiCl = 2Bi + BiCl_3 ; \text{ compare } AuCl = 2Au + AuCl_3.$$

33. ARSENIC. As = 74·96.

Occurrence.

Arsenic is found as sulphides in the form of REALGAR, AsS, and ORPIMENT, As_2S_3, the latter being analogous to Sb_2S_3 and Bi_2S_3, although it differs considerably from them in its crystalline constants

The principal source of arsenic is, however, ARSENICAL PYRITES, the presence of arsenic in pyrites being so frequent as to be almost universal. It is noteworthy that in pyrites arsenic replaces sulphur atom for atom; thus, the most important arsenical mineral is MISPICKEL, FeSAs, which is similar in its crystalline form to marcasite, FeS_2; again, the two arsenides, $CoAs_2$ and $NiAs_2$, are both dimorphous, like iron pyrites, FeS_2, one form resembling pyrites and the second form resembling marcasite. Native arsenic is also found both alone and as an impurity in antimony and bismuth, with which it is isomorphous.

Preparation and Properties of Arsenic.

(*a*) *Preparation.*—Metallic arsenic is prepared by reducing arsenious oxide with carbon,

$$As_4O_6 + 3C = As_4 + 3CO_2.$$

The metal is obtained as a crystalline sublimate in the upper part of the crucible. It can also be prepared on a large scale by distilling arsenical pyrites,

$$FeSAs = FeS + As.$$

(*b*) *Physical Properties.*—Arsenic is a crystalline element of density 5·7, with a dull metallic lustre and marked metallic conductivity. It melts at 817° when heated under pressure or in a sealed tube, but usually sublimes without melting. The density of the yellow vapour corresponds with the formula As_4, just as in the case of phosphorus, the gaseous molecules of which are represented by the formula P_4.

(*c*) *Allotropy.*—A non-metallic form of arsenic can be obtained by the rapid condensation of the vapour from a stream of hydrogen or carbon dioxide (compare yellow phosphorus). It is yellow in colour, dissolves in carbon disulphide, and is much lighter than metallic arsenic, to which it reverts readily under the influence of light, or when heated. Its molecular weight in solution corresponds with the formula As_4. A brown and a grey form of arsenic have also been described.

(*d*) *Chemical Properties.*—Arsenic is stable in air at atmospheric temperatures, but when heated burns readily to the oxide, As_4O_6. It combines directly with chlorine to form arsenious chloride, $AsCl_3$, and is usually converted into the hydride, arsine, AsH_3, when hydrogen is generated in contact with the metal or its compounds.

(*e*) *Valency.*—Arsenic exhibits considerable variations of valency. In its principal compounds it is *tervalent*, as in AsH_3, $AsCl_3$, As_4O_6, etc. It is, however, *quinquevalent* in the pentoxide, As_2O_5, and in the arsenates derived from it, *e.g.*, Na_3AsO_4, which are isomorphous with the phosphates: quinquevalent halogen derivatives such as the iodide, AsI_5, compare PCl_5, have also been prepared. In realgar, AsS, and in arsenical pyrites, FeSAs, arsenic is probably *bivalent*.

Arsine or **Arseniuretted Hydrogen,** AsH_3.

Metallic arsenic does not combine directly with hydrogen gas, but arsine, AsH_3, is formed when hydrogen is generated, either by the action of acids on metals or by electrolysis, in contact with solutions containing arsenic.

It is a colourless gas with highly poisonous properties; it condenses to a liquid which boils at $-55°$ and freezes at about $-115°$. It is decomposed by heating,

$$4AsH_3 = As_4 + 6H_2,$$

depositing metallic arsenic as in Marsh's test for arsenic (p. 706). In a limited supply of air it burns to metallic arsenic and water, but in an excess of air arsenious oxide and water are formed. Arsine can be removed from a gas by passing it through a solution containing a soluble silver salt; the essential action is the oxidation shown in the equation

$$4AsH_3 + 12Ag_2O = As_4O_6 + 24Ag + 6H_2O.$$

Halogen Derivatives of Arsenic.

Arsenious chloride, $AsCl_3$, is prepared by the direct action of chlorine on metallic arsenic,

$$As_4 + 6Cl_2 = 4AsCl_3;$$

it is also formed by the action of strong hydrochloric acid or of a mixture of sulphuric acid and common salt on arsenious oxide,

$$As_4O_6 + 12HCl = 4AsCl_3 + 6H_2O.$$

The anhydrous compound is a liquid which boils at 130° and when frozen melts at $-18°$. In presence of an excess of water, arsenious oxide is precipitated, but arsenious chloride can be distilled from a mixture of the oxide and strong hydrochloric acid; the action shown in the last equation is therefore reversible,

$$As_4O_6 + 12HCl \rightleftharpoons 4AsCl_3 + 6H_2O.$$

The gradation of properties in the other halogen derivatives of arsenic is shown in the following table:

TABLE 79.—HALOGEN-DERIVATIVES OF ARSENIC.

Tervalent Compounds.			*Quinquevalent Compounds.*		
	Melting-point.	*Boiling-point.*		*Melting-point.*	*Boiling-point.*
AsF_3 ..	—	+ 63°	AsF_5 ..	− 80°	− 53°
$AsCl_3$ ..	− 18°	+ 130°	$AsCl_5$ ..	− 40°	—
$AsBr_3$ ..	+ 31°	+ 220°	$AsBr_5$ ..	—	—
AsI_3 ..	+ 146°	about 400°	AsI_5 ..	+ 70°	—

Arsenic trifluoride, AsF_3, prepared by distilling arsenious oxide and fluorspar with sulphuric acid (compare SiF_4), is a fuming liquid which attacks glass (compare HF and NH_4F) and is decomposed by water into arsenious and hydrofluoric acids, but unites with ammonia to form a crystalline compound, probably $AsF_3,5NH_3$.

Arsenic pentafluoride, AsF_5, prepared by the action of bromine and antimony pentafluoride on arsenic trichloride, is a colourless gas which condenses at $-53°$ to a yellow liquid and freezes at $-80°$ to a white mass. It attacks glass only in presence of a trace of moisture or of hydrogen fluoride. Silicon and most metals liberate arsenic and form fluorides. The gas has the normal composition and vapour density for the formula AsF_5.

Arsenic pentachloride, $AsCl_5$, is prepared by saturating the trichloride with chlorine at low temperatures, and distilling off the excess of chlorine at $-31°$; it crystallises on cooling alone, or from solution in carbon disulphide or ether, in yellow prisms (compare PCl_5), melting at about $-40°$, but begins to decompose at $-25°$.

Arsenic tribromide, $AsBr_3$, prepared by direct combination of the two elements, forms colourless prisms melting at 20°; it boils at 220° and is the only compound of these elements that is known.

Arsenic di-iodide, AsI_2, can be sublimed from a mixture of iodine and arsenic; it crystallises in cherry-red prisms and decomposes slowly into arsenic and the tri-iodide.

Arsenic tri-iodide, AsI_3, also prepared by direct combination, forms red tablets, melts at 146°, and boils at 394–414°; when acted on by more iodide at 150° it gives **arsenic pentaiodide,** AsI_5, a brown solid melting at 70°.

Arsenic and Oxygen.

Arsenious oxide or **white arsenic,** As_4O_6, is prepared by roasting arsenical ores such as pyrites and condensing the volatile arsenious oxide in a series of chambers or flues which are cleared at intervals of a few weeks. The crude product can be purified by resubliming it from a reverberatory furnace heated by means of anthracite or coke.

A vitreous form of the oxide, known as ARSENIC GLASS, is obtained by subliming refined arsenic in a closed vessel, *e.g.*, in a pot with a capacious cover, instead of in the draught of a furnace. This form of arsenic, which has a lower density than the crystals, gradually becomes crystalline and opaque, the change of state extending progressively from the outside to the inside of the lumps.

The oxide is dimorphous, the stable form consisting of octahedral crystals belonging to the cubic system; the less stable monosymmetric form separates from alkaline solutions of the oxide, is deposited sometimes from the vapour, and has been found as a mineral. The oxide is sparingly soluble in water, which dissolves about 10 per cent. of the crystals at 100°; the solubility at 15° is about $1\frac{1}{2}$ per cent., but the vitreous from is said to be more soluble than the crystals. It sublimes without melting at about 200°; the density of the vapour corresponds with the formula As_4O_6.

Arsenious oxide is amphoteric in character, since it can be converted by the action of hydrochloric acid into arsenious chloride (p. 702) although alkalies convert it even more readily into arsenites in which the arsenic is the acid-forming element :

$$As_4O_6 + 12HCl = 4AsCl_3 + 6H_2O.$$
$$As_4O_6 + 12NaOH = 4Na_3AsO_3 + 6H_2O.$$

The oxide is highly poisonous but can be tolerated in relatively large quantities by those who are accustomed to taking it ; a number of derivatives have been prepared which can be tolerated in still larger doses, although they retain their toxicity towards lower organisms ; these compounds, as well as the oxide, are largely used in medicine. The poisonous qualities of the oxide are made use of in rat poisons, and in sheep dips, which usually contain arsenious oxide dissolved in an alkali. The oxide is also employed in the preparation of pigments and enamels and as a mordant in dyeing, and is used extensively as a preservative, especially for wood. In pyrotechny it is used to produce a white fire.

In view of the wide distribution of arsenic in coal and coke, as well as in sulphuric acid prepared by the chamber process, traces of arsenic are present in many products, and may find their way into substances which are used as foodstuffs ; the detection and estimation of small quantities of arsenic are therefore of exceptional importance.

The ARSENITES are salts of the hypothetical arsenious acid, H_3AsO_3. **Sodium arsenite,** Na_3AsO_3, is perhaps contained in solutions (such as sheep dips) prepared by dissolving arsenious oxide in sodium carbonate, and has been isolated from alcoholic solutions of arsenious oxide in sodium hydroxide, but the salts which separate from solution contain a larger proportion of arsenic and have the composition of a **meta-arsenite,** $NaAsO_2$, or a complex **tetrarsenite,** $Na_2As_4O_7,2H_2O$ (compare $NaBO_2$ and $Na_2B_4O_7$, p. 519). **Copper arsenite,** $CuHAsO_3$, is prepared by double decomposition from copper sulphate and arsenious oxide dissolved in potassium carbonate ; it is soluble in acids or in an excess of alkali, and was formerly used as a pigment under the name of SCHEELE'S GREEN ; a mixed acetate and arsenite of copper, prepared from basic copper acetate (verdigris) and arsenious oxide, is known as SCHWEINFURT GREEN.

Arsenic oxide, As_2O_5 (or perhaps As_4O_{10}, to correspond with P_4O_{10}), prepared by oxidising white arsenic with boiling nitric acid or by the action of chlorine water, is obtained as a deliquescent solid by evaporating the solution. It forms a series of ARSENATES which are isomorphous with the corresponding phosphates. The most important of these is **sodium arsenate,** Na_2HAsO_4, corresponding with sodium phosphate ; this can be prepared by oxidising crude sodium arsenite by heating it with sodium nitrate, and is used in calico-printing.

Sulphides of Arsenic.

Arsenic monosulphide, AsS, is found as the mineral REALGAR and can be prepared in a crude state by heating a mixture of iron pyrites and arsenical pyrites,

$$FeS_2 + FeSAs = 2FeS + AsS.$$

It can also be prepared by the direct combination of arsenic and sulphur.

Realgar burns to arsenious oxide and sulphur dioxide. Chlorine converts it into chlorides of sulphur and arsenic,

$$2AsS + 4Cl_2 = 2AsCl_3 + S_2Cl_2,$$

but with iodine it forms an additive compound, AsSI. Realgar when heated changes from the red to a black modification at 267°, melts at 307°, and boils at 565°. It is used as a pigment and in pyrotechny.

Arsenic sesquisulphide, As_2S_3, is found as the mineral ORPIMENT. It can be prepared by subliming a suitable mixture of arsenic and sulphur, or can be precipitated as a yellow powder by passing sulphuretted hydrogen into an acid solution of arsenious oxide, *e.g.*,

$$2AsCl_3 + 3H_2S = As_2S_3 + 6HCl.$$

The sesquisulphide changes from the yellow to a red modification at 170°, melts at 300°, and boils at 707°. Unlike antimony sulphide, Sb_2S_3, and stannic sulphide, SnS_2, it does not dissolve in concentrated hydrochloric acid, but it is oxidised by and dissolves in concentrated nitric acid, and dissolves readily in alkaline sulphides, forming THIOARSENITES, *e.g.*, **potassium thiometarsenite,** $KAsS_2$,

$$As_2S_3 + K_2S = 2KAsS_2.$$

It also dissolves in alkalies, giving a mixture of a metarsenite and thiometarsenite, from which it is reprecipitated by the addition of acids :

$$2As_2S_3 + 4KOH = KAsO_2 + 3KAsS_2 + 2H_2O.$$
$$KAsO_2 + 3KAsS_2 + 4HCl = 2As_2S_3 + 4KCl + 2H_2O.$$

Cuprous thioarsenite, Cu_3AsS_3, and **silver thioarsenite,** Ag_3AsS_3, derived from *ortho*-thioarsenious acid, H_3AsS_3, are found as minerals.

Diarsenic pentasulphide, As_2S_5, is formed as a red precipitate by the action of hydrochloric acid on a thioarsenate, *e.g.*,

$$2Na_3AsS_4 + 6HCl = As_2S_5 + 6NaCl + 3H_2S.$$

It is insoluble in water, but dissolves in alkaline sulphides, forming THIOARSENATES, *e.g.*, **sodium thioarsenate,** Na_3AsS_4 ; these can be prepared readily by the action of sodium sulphide on a mixture of the sesquisulphide, As_2S_3, and sulphur,

$$3Na_2S + As_2S_3 + S_2 = 2Na_3AsS_4,$$

and are themselves the source from which the pentasulphide is derived.

Detection and Estimation of Arsenic.

On account of its wide distribution and its very poisonous properties, the detection and estimation of arsenic are of exceptional importance.

The dry tests for arsenic include the garlic-like odour which is noticed when the metal is vaporised in air, and the foul smell of **cacodyl oxide,** $(CH_3)_2As{\cdot}O{\cdot}As(CH_3)_2$, produced by heating compounds of arsenic with sodium acetate. The production of a mirror of the metal and of minute crystals of the volatile oxide are also characteristic properties.

Arsenious compounds give with sulphuretted hydrogen a yellow precipitate of **arsenious sulphide,** As_2S_3, which is soluble in ammonia, in ammonium sulphide, and in ammonium carbonate, but is reprecipitated by hydrochloric acid. In neutral solutions silver nitrate gives a yellow precipitate of **silver arsenite,** Ag_3AsO_3, whilst copper gives a green precipitate of **copper arsenite** or Scheele's green, $CuHAsO_3$; these two compounds are readily soluble in acids and in ammonia.

Arsenic compounds can be distinguished from arsenious compounds by the formation of a reddish-brown **silver arsenate,** Ag_3AsO_4, which is precipitated more readily than the yellow arsenite, Ag_3AsO_3, when an acid solution of silver nitrate containing arsenic in solution is gradually neutralised with ammonia. Copper sulphate precipitates a bluish-green **copper arsenate,** $Cu_3(AsO_4)_2$ (compare copper phosphate). Arsenates are also precipitated, like the phosphates, by means of ammonium molybdate dissolved in nitric acid, and as **ammonium magnesium arsenate,** NH_4MgAsO_4, by magnesium salts in presence of ammonium chloride. With sulphuretted hydrogen quinquevalent arsenic compounds give a precipitate of sulphur together with **arsenious sulphide,** As_2S_3. Arsenites and arsenates can also be distinguished by the reducing action of the former on iodine, potassium dichromate, and potassium permanganate, and by the oxidising action of the latter upon sulphurous acid, etc.

In REINSCH'S TEST for arsenic the metal is deposited as a **copper arsenide,** perhaps as As_2Cu_5, on the surface of metallic copper by boiling it for a considerable time with hydrochloric acid; the arsenic may be identified by subliming it from the copper in the form of the oxide.

In MARSH'S TEST, which is the standard method of detecting and estimating minute traces of arsenic, hydrogen is liberated by the action of zinc or magnesium on acids, or electrolytically, and the arsenic is converted into the hydride, AsH_3.* Under these conditions antimony is also carried forward as the hydride, SbH_3, but in the electrolytic form of the test it can be retained, as Sb_2S_3, by precipitating it with sulphuretted hydrogen. The presence of arsenic in the gas can be detected by passing it through a heated tube, when a mirror of metallic arsenic is deposited; the magnitude of the deposit can be used to esti-

* Arsenates are not reduced to arsine by electrolysis with a platinum cathode unless first reduced to arsenites, *e.g.*, by $K_2S_2O_5$; but with a lead cathode reduction to arsine can be effected in one operation.

mate small traces of arsenic, and the deposit can be distinguished from antimony (i) by the fact that it dissolves readily in sodium hypochlorite, and (ii) by the fact that when dissolved in dilute nitric acid it gives a solution from which silver nitrate throws down the yellow arsenite, Ag_3AsO_3. Arsenic can also be detected by passing the gas into aqueous silver nitrate, when metallic silver is thrown down, whilst arsenic remains in solution and can be detected by neutralising with ammonia and thus precipitating yellow silver arsenite; this action may be represented by the equation

$$4AsH_3 + 24AgNO_3 + 6H_2O = As_4O_6 + 24Ag + 24HNO_3.$$

Stibine also precipitates silver from silver nitrate, but the antimony is thrown down as $SbAg_3$ instead of remaining in solution.

Arsenic is estimated gravimetrically by precipitating it as **ammonium magnesium arsenate,** $NH_4MgAsO_4,6H_2O$, which may be weighed as such by drying at atmospheric temperatures, or may be dried at 100° to 110° to $NH_4MgAsO_4,\frac{1}{2}H_2O$, or finally ignited and weighed as **magnesium pyroarsenate,** $Mg_2As_2O_7$. Arsenic may also be weighed as the **sesquisulphide,** As_2S_3.

The volumetric estimation of arsenic depends on the oxidation of the arsenite to the arsenate by means of iodine, potassium dichromate, or potassium permanganate.

The atomic weight of arsenic is based mainly upon determinations of the ratios $3As_4O_6 : 4KClO_3$, $AsCl_3 : 3Ag$, and $Ag_3AsO_4 : 3AgCl : 3AgBr$.

51. Antimony. Sb = 120·2.

Occurrence.

Native antimony, generally containing isomorphous arsenic, is one of the minor sources of antimony, and **oxides,** probably formed

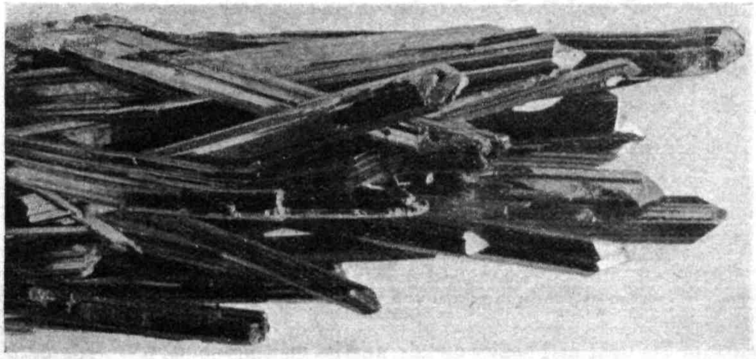


FIG. 251.—CRYSTALS OF STIBNITE. (British Museum, Natural History.)

by oxidation of sulphide ores, are also found occasionally. The most important ore of antimony is, however, **antimony sulphide,** Sb_2S_3, a

grey or black mineral with a brilliant metallic lustre, which has long been known as STIBNITE or ANTIMONITE (Fig. 251), and was formerly used for blackening the eyebrows. **Cuprous thioantimonite,** $3Cu_2S,Sb_2S_3$ or Cu_3SbS_3, isomorphous with cuprous thioarsenite, Cu_3AsS_3, and **silver thioantimonite,** $3Ag_2S,Sb_2S_3$, or Ag_3SbS_3, isomorphous with silver thioarsenite, Ag_3AsS_3, are of some importance as ores of copper and silver respectively. Antimony may also replace sulphur in mineral sulphides, *e.g.*, NiSbS crystallises in striated cubes like iron pyrites, FeS_2, and is also isomorphous with cobaltite, CoAsS, and with the cubic form of NiAsS.

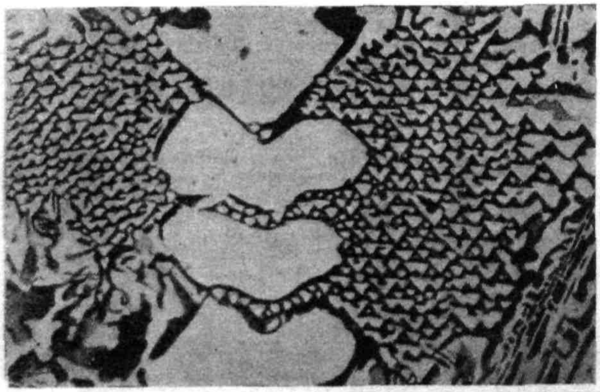
Metallic Antimony.

(*a*) *Preparation.*—Metallic antimony is prepared by reducing the sulphide with iron,

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS;$$

the sulphide of iron forms a slag and floats on the molten metal. The crude metal, which may contain iron, sulphur, and arsenic (the two former mainly as ferrous sulphide), is purified by heating it repeatedly with salts of the alkali metals, such as sodium sulphate and potassium carbonate, together with some of the iron sulphide slag, mainly in order to remove arsenic, which passes more readily than antimony into the acid radical of the sodium or potassium salt, *e.g.*, as thioarsenite.

(*b*) *Physical Properties.*—Antimony is a coarsely crystalline metal with a brilliant lustre. Its density, 6·62, is intermediate between



×200 FIG. 252.—ANTIMONY AND COPPER. *Desch.*
Antimony (white, in excess) with Copper Antimonide, Cu_2Sb (black, as eutectic alloy).

those of the light and heavy metals, and its melting-point, 630° (compare magnesium, m.p. 650°, and aluminium, m.p. 657°), is intermediate between those of the fusible metals, zinc, lead, cadmium, tin, and bismuth, on the one hand, which melt between 200° and 400°, and copper, silver, and gold on the other, which melt in the neighbourhood

of 1000°. Antimony boils at 1440°, the density of the vapour being rather less than that required for the formula Sb_2.

Antimony is a brittle metal, which forms a large number of intermetallic compounds. In some of these it behaves as a bivalent element like sulphur, *e.g.*,

Cu_2Sb (Fig. 252); CaSb,NiSb,CoSb,ZnSb,CdSb; $FeSb_2$, $PtSb_2$;

but in others it acts as a tervalent or quinquevalent element, *e.g.*,

Cu_3Sb, Ag_3Sb; Mg_3Sb_2,Zn_3Sb_2,Cd_3Sb_2,Fe_3Sb_2; Ni_5Sb_2.

It forms solid solutions with bismuth and tin, but is very limited in this respect; even as a liquid it does not mix freely with arsenic below 600°. In its alloys it is generally used, like carbon in iron, as a hardening element. Metallic antimony possesses the property of expanding when it crystallises; this property, which is shared by the alloys of antimony, is of considerable value in casting.

FIG. 253.—EXPLOSIVE ANTIMONY.

(*c*) *Allotropy.*—A yellow non-metallic form of antimony has been described (compare arsenic), but more remarkable perhaps is the EXPLOSIVE ANTIMONY (Fig. 253) obtained by depositing antimony electrolytically from concentrated solutions of a halogen salt such as antimony trichloride, $SbCl_3$. The grey metallic deposit, which explodes violently when heated to 200°, is not a pure metal, since it always contains halogen as well as metal, the proportion increasing with the concentration of the solution from which it is deposited; it has therefore been suggested that the explosive product is a solid solution of antimony chloride (or bromide or iodide) in the metal, the metal being perhaps forced over by the halogen salt into a different crystalline form of much lower stability.

(*d*) *Alloys of Antimony.*—TYPE METAL is an alloy of lead containing 13 to 30 per cent. of antimony, and sometimes also tin or bismuth up to about 20 per cent. The antimony, producing a tendency to expand on solidification, lowers the melting-point and increases the hardness of the metal. Linotype metal may be regarded as the eutectic alloy of lead and antimony (Pb 87 per cent., Sb 13 per cent., m.p. 246°) to which 2 per cent. of tin has been added.

BRITANNIA METAL is tin hardened with 5 to 10 per cent. of antimony. The alloy, which melts at about 250°, is perhaps an isomorphous mixture of antimony and tin, and is used extensively in the manufacture of plated goods. The addition of copper has the effect of colouring the metal.

BEARING METALS such as BABBIT'S METAL, which are used for the bearings of shafting and of machines, usually consist of tin together with both antimony and copper, *e.g.*, tin 85 per cent., antimony 10 per cent., copper 5 per cent. ; under these conditions an **antimonide,** SnSb, is formed, and the alloy consists of hard crystals of this compound embedded in a matrix of soft metallic tin.

(*e*) *Chemical Properties of Antimony.*—Metallic antimony is stable in air, but burns to the oxide, SbO_2, when heated ; it also burns in chlorine gas to the trichloride, $SbCl_3$, and combines with sulphur and phosphorus when heated. It does not unite directly with hydrogen, nitrogen, or carbon, but the hydride, SbH_3, can be prepared by generating hydrogen in contact with the metal. Dilute hydrochloric and dilute sulphuric acids have no action upon it, but it is oxidised by steam at a red heat and by nitric acid. It dissolves in hot strong hydrochloric acid when air is present, forming the chloride ; it also dissolves in concentrated sulphuric acid, forming the sulphate. The oxides are amphoteric, forming salts both with acids and with bases.

Antimony and Hydrogen.

Stibine or **antimoniuretted hydrogen,** SbH_3, is formed, like arsine, by generating hydrogen in contact with metallic antimony or its compounds. It is a colourless gas which is readily decomposed by heating, depositing a mirror of the metal. The pure compound melts at $-88°$ and boils at $-17°$. The gas is very poisonous, and burns in air with liberation of white fumes of the oxide.

Chlorides of Antimony.

Antimony trichloride, or BUTTER OF ANTIMONY, $SbCl_3$, was prepared at an early period by heating the sulphide with mercuric chloride,

$$Sb_2S_3 + 3HgCl_2 = 3HgS + 2SbCl_3.$$

It can also be prepared by the action of chlorine on the metal or its sulphide. It is a crystalline compound melting at 73° and boiling at 223°. It dissolves in a small quantity of water, or in presence of hydrochloric acid, but on dilution is precipitated as a basic chloride, POWDER OF ALGAROTH, the principal constituent of which is an **oxychloride,** SbOCl. When antimony sulphide is heated with strong hydrochloric acid, water and hydrochloric acid come over first, and finally anhydrous antimony trichloride distils. The anhydrous chloride combines with ammonia to form a compound, $SbCl_3,NH_3$, compare $SiF_4,2NH_3$ (p. 489), etc., which dissociates when heated.

Antimony pentachloride, $SbCl_5$, prepared by passing chlorine into the molten trichloride, melts at 4° and is therefore liquid at atmospheric temperatures ; when heated, it breaks down into the trichloride and chlorine, but it can be distilled under reduced pressure without

decomposition. With water it forms the hydrates, $SbCl_5,H_2O$ and $SbCl_5,4H_2O$, but is decomposed by hot water, giving the hydrated oxide, **antimonic acid**, Sb_2O_5 aq. It combines with SCl_4, PCl_5, $POCl_3$, etc., and forms double chlorides derived from **chlorantimonic acid**, $HSbCl_6$, a compound which crystallises out with $4\frac{1}{2}H_2O$ when a solution of antimony trichloride is saturated with chlorine and hydrogen chloride.

Antimony tetrachloride (compare $BiCl_4$), intermediate between the two preceding compounds, is not known in the free state, but **double salts,** *e.g.*, Rb_2SbCl_6, have been prepared by mixing the trichloride and pentachloride with an alkali chloride in presence of hydrochloric acid.

Compounds of the type SbX_3 and SbX_5 containing other halogens are known, but the existence of the pentabromide and pentaiodide is doubtful.

Antimony and Oxygen.

Antimonious oxide, Sb_4O_6.—This compound is found as a mineral in two different crystalline forms which are isomorphous with two mineral forms of arsenious oxide, As_4O_6. It is the principal product formed on burning the metal or its sulphide in air; it can also be prepared by acting on antimony with sulphuric or nitric acid, when an unstable sulphate or nitrate is probably formed, and converting the product into the oxide by the action of hot water and dilute alkali.

Antimonious oxide is a colourless (or dull brown) compound. It melts at a red heat and solidifies to a crystalline mass. It is more volatile than the higher oxides and can be separated from them by sublimation; its vapour density corresponds with the formula Sb_4O_6.

Antimonious oxide is reduced to the metal by heating it in a current of hydrogen, and oxidises in air to the tetroxide, Sb_2O_4. It dissolves in hydrochloric acid to form the trichloride, and in solutions of potassium hydrogen tartrate, $KH(C_4H_4O_6)$, to form **potassium antimonyl tartrate,** $K(SbO)(C_4H_4O_6)$, a compound which has long been known and used in medicine under the name of TARTAR EMETIC. It does not dissolve in dilute nitric or sulphuric acid, but fuming nitric acid and fuming sulphuric acid give a **basic nitrate** of the formula Sb_4O_6,N_2O_5, and a **basic sulphate** of the formula $Sb_4O_6,2SO_3$ or $(SbO)_2SO_4$; the **trisulphate,** $Sb_2(SO_4)_3$, has been crystallised out by concentrating the solutions prepared by dissolving the oxide or sulphide in sulphuric acid.

Antimonious oxide dissolves readily in alkalies, forming a series of ANTIMONITES, *e.g.*, **sodium metantimonite,** $NaSbO_2,3H_2O$, which crystallises out from the aqueous solutions obtained by dissolving the oxide in sodium hydroxide. Hydrated forms of the oxide having the composition of **antimonious acid,** H_3SbO_3, and **pyroantimonious acid,** $H_4Sb_2O_5$, have been described, but the meta-acid, $HSbO_2$, is only known in the form of its salts.

Diantimony tetroxide, Sb_2O_4, is found native as ANTIMONY OCHRE. It is formed by heating the preceding oxide in air and by the oxidising action of nitric acid on the metal, on antimonious oxide, or on the sesquisulphide. It is a colourless powder which becomes yellow on heating. At moderate temperatures it is the most stable of the oxides of antimony, but on stronger heating it loses oxygen and is converted into the more volatile antimonious oxide. It does not dissolve to any marked extent in water, but has an acid reaction towards litmus. It has no obvious basic properties and does not form metallic salts with acids, although, as stated above, the tetrachloride, $SbCl_4$, is known as a double salt; on the other hand, it combines with bases to form salts of the type $K_2Sb_2O_5$ (contrast $H_4P_2O_6$, p. 430), two of which, $CaSb_2O_5$ and $CuSb_2O_5$, have been found as minerals.

Antimonic oxide, Sb_2O_5, is obtained by the action of nitric acid on the metal or on the lower oxides, the product being heated gently to decompose any traces of basic antimonious nitrate that may be formed. It is a yellow powder with an acid reaction to litmus. Hydrates corresponding with the formulæ of **orthoantimonic acid,** H_3SbO_4, **pyroantimonic acid,** $H_4Sb_2O_7,2H_2O$, and **metantimonic acid,** $HSbO_3$, have been prepared. Salts derived from orthoantimonic acid do not appear to be known, but a considerable number of salts of the meta- and pyro-acids have been described: the four anhydrous compounds described below are important in that their composition and character are quite definite; in the case of the hydrated compounds it is difficult or impossible to decide from which of the three forms of the acid the salts are derived. The METANTIMONATES include the anhydrous **ammonium** and **lead salts,** $(NH_4)SbO_3$ and $Pb(SbO_3)_2$, and the hydrated **potassium** and **sodium salts,** $KSbO_3$, aq and $NaSbO_3$, aq. The potassium salt has been used as a reagent for sodium, since with sodium chloride it yields a sodium antimonate, $Na_2H_2Sb_2O_7,6H_2O$ (or perhaps $2NaSbO_3,7H_2O$), generally known as **sodium metantimonate,** which is one of the least soluble salts of sodium (1 part in 350 parts of water). Two PYROANTIMONATES, namely **calcium pyroantimonate,** $Ca_2Sb_2O_7$, and **ferrous pyroantimonate,** $Fe_2Sb_2O_7$, are known as minerals.

Antimony and Sulphur.

Antimony sesquisulphide, Sb_2S_3, well known as the mineral STIBNITE or ANTIMONITE (Fig. 249), is remarkable for its brilliant metallic lustre, its black colour, and its low melting-point, about 555°, which makes it possible to concentrate the mineral by fusion. The sesquisulphide is thrown down as an orange-red precipitate (perhaps hydrated) by the action of sulphuretted hydrogen on acid solutions of antimony trichloride or of tartar emetic; when heated to 200° it loses water and becomes black.

Antimony sesquisulphide dissolves readily in alkaline sulphides to form THIOANTIMONITES, *e.g.*, **sodium thioantimonite,** Na_3SbS_3.

Caustic alkalies give a mixture of thiometantimonite and metantimonite, *e.g.*,

$$2Sb_2S_3 + 4KOH = 3KSbS_2 + KSbO_2 + 2H_2O,$$

from which the sulphide is reprecipitated by acids (compare arsenic). The crude sulphide obtained by boiling stibnite with alkalies and allowing the clear solution to cool acquired at one time a high reputation in medicine under the name of KERMES MINERAL. **Cuprous thioantimonite,** Cu_3SbS_3, and **silver thioantimonite,** Ag_3SbS_3, have already been referred to as minerals which are isomorphous with the corresponding thioarsenites.

Antimony disulphide, SbS_2, or **diantimony tetrasulphide,** Sb_2S_4, is obtained as a yellowish-red precipitate on acidifying an aqueous solution of a THIOANTIMONATE, *e.g.*, **potassium thioantimonate,** K_3SbS_4, prepared by dissolving a mixture of stibnite and sulphur in an alkali or in an alkaline sulphide :

$$Sb_2S_3 + S_2 + 3K_2S = 2K_3SbS_4,$$
$$2K_3SbS_4 + 6HCl = 6KCl + Sb_2S_4 + S + 3H_2S;$$

it can also be precipitated in an impure form, mixed with the sesquisulphide and with sulphur, by the action of sulphuretted hydrogen on an acid solution of a quinquevalent compound of antimony. When heated gently it decomposes into the black sesquisulphide and sulphur, and a similar decomposition takes place under the action of hydrochloric acid, which liberates sulphur and converts it into the trichloride,

$$Sb_2S_4 + 6HCl = 2SbCl_3 + S + 3H_2S.$$

It dissolves readily in alkaline sulphides, forming thioantimonates and thioantimonites, *e.g.*,

$$Sb_2S_4 + 3Na_2S = Na_3SbS_4 + Na_3SbS_3,$$

and in alkalies (including sodium and potassium carbonates and ammonia, but not ammonium carbonate), forming thioantimonates, antimonates, etc. **Cuprous thioantimonate,** Cu_3SbS_4, is found as a mineral, and the compound Sb_2S_4 is perhaps an **antimony thioantimonate,** $SbSbS_4$; but the pentasulphide, Sb_2S_5 (corresponding with diarsenic pentasulphide, As_2S_5), from which these compounds are derived, is not known in a free state.

Detection and Estimation of Antimony.

When heated on charcoal with sodium carbonate and potassium cyanide, compounds of antimony yield a brittle metallic bead. They impart a green colour to the reducing flame, but in an oxidising flame burn to the white oxide, which can be deposited on a cold surface and identified by giving a black product by the action of silver nitrate and ammonia.

Antimonious compounds give with sulphuretted hydrogen in acid

solutions an orange-red precipitate of **antimony sesquisulphide,** Sb_2S_3, which differs from As_2S_3 in being insoluble in aqueous solutions of ammonium carbonate; it dissolves, however, in caustic alkalies, including ammonia, and in alkaline sulphides; it is insoluble in dilute acids, but dissolves in strong hydrochloric acid. Caustic alkalies give with soluble antimonious salts a precipitate of the **hydroxide,** $Sb(OH)_3$, which is soluble in an excess of the reagent.

Quinquevalent compounds of antimony give with hydrogen sulphide an orange-red precipitate of **antimony disulphide** and sulphur, which dissolves in alkalies and in alkaline sulphides. They can be distinguished from the tervalent compounds by their oxidising action upon iodides, whereby iodine is liberated, and by the absence of any reducing action on chromates and permanganates.

Metallic antimony is deposited from acid solutions on platinum foil in contact with metallic zinc; the metal is insoluble in cold dilute hydrochloric acid, but dissolves in nitric acid or in tartaric acid, and can be recognised by reprecipitating it as the red sesquisulphide. Antimony can also be detected by Marsh's test (p. 706).

Antimony is usually estimated as Sb_2S_3, which may be weighed as such, or converted into Sb_2O_4 by the action of nitric acid. Volumetric analysis, as in the case of arsenic, depends on oxidising the antimonite to the antimonate by means of iodine or of potassium permanganate.

The atomic weight of antimony is based on determinations of the ratios $Sb_2 : Sb_2S_3$, $SbBr_3 : 3Ag$, $SbBr_3 : 3AgBr$ and $SbI_3 : 3AgI$.

83. BISMUTH. Bi = 208·0.

Occurrence.

Bismuth is found most frequently as native metal, which may be contaminated with isomorphous antimony and arsenic. The **sesquisulphide,** Bi_2S_3, or BISMUTHITE, is a rare mineral, isomorphous with stibnite and possessing a similar brilliant metallic lustre.

Metallic Bismuth.

(*a*) *Preparation.*—Native bismuth is separated from non-metallic impurities by melting and running off the metal. It can be refined by melting it under fused potassium nitrate, in order to eliminate arsenic and antimony in the form of potassium arsenate or antimonate. The pure metal can be prepared by using metal formed by reduction of the precipitated oxide instead of native bismuth for the refining process.

(*b*) *Physical Properties.*—Metallic bismuth is a heavy metal of density 9·8, which melts very readily at 271°, and on cooling forms beautifully tarnished crystals resembling skeletal cubes (Fig. 254). It boils at 1420°, *i.e.*, 20° below the boiling-point of antimony; its vapour-density is a little lower than that calculated for the formula Bi

(c) *Alloys of Bismuth.*—Bismuth is used mainly in the manufacture of fusible alloys (p. 684), including—

	Bi	Pb	Sn	Cd	Melting-point.
Rose's Alloy	2	1	1	—	94°
Wood's Alloy	4	2	1	1	71°

These alloys are used for casting (*e.g.*, in dentistry for making dies to use in "swaging" gold plates, which are hammered to the correct

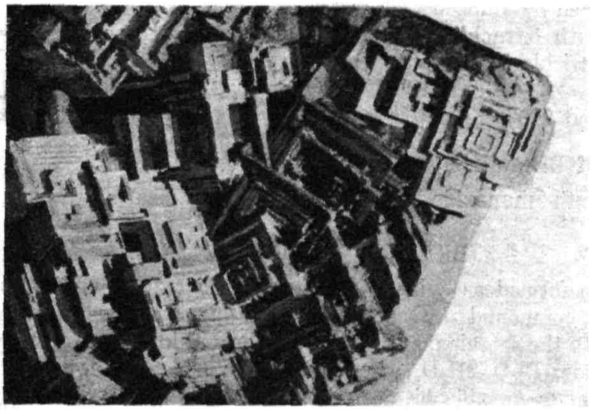


FIG. 254.—METALLIC BISMUTH.

shape between a die of fusible alloy and a soft counter-die of lead) and in fire-protection systems for closing automatic sprinklers. Rose's alloy is of interest in that it is said to contract between 95° and 131°, but to expand when heated above or below this range of temperatures.

(*d*) *Chemical Properties.*—Bismuth burns in air to the oxide, Bi_2O_3, and decomposes steam at a red heat. It is but little acted upon by hydrochloric acid, but dissolves readily in nitric acid, forming the nitrate, $Bi(NO_3)_3$; with hot strong sulphuric acid it yields a basic sulphate. When hydrogen is prepared in contact with bismuth minute traces (about 1 part in 50,000) of a **hydride** are formed, presumably BiH_3.

Chlorides of Bismuth.

Bismuth monochloride, BiCl, prepared by direct combination of bismuth and chlorine, decomposes and breaks down into two layers (perhaps $3BiCl = 2Bi + BiCl_3$, compare $3AuCl = 2Au + AuCl_3$) when heated to 318°.

Bismuth dichloride, $BiCl_2$, has been described as a black solid, prepared by heating together mercurous chloride and bismuth,

$$Hg_2Cl_2 + Bi = BiCl_2 + 2Hg.$$

The evidence for its existence as a distinct compound is, however, not very convincing, and it may be a mixture of Bi or BiCl with $BiCl_3$.

Bismuth trichloride, $BiCl_3$, is prepared by the action of chlorine on metallic bismuth; a yellow liquid is formed from which crystals of the trichloride can be sublimed; these melt at about 232° and boil at about 447°. By the action of water, bismuth trichloride yields **bismuth oxychloride** and hydrochloric acid; the action

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

is reversible, the oxychloride being dissolved by adding acid and re-precipitated by dilution with water.

Bismuth tetrachloride, $BiCl_4$, is prepared by the action of chlorine on the trichloride,

$$2BiCl_3 + Cl_2 = 2BiCl_4.$$

It melts at 226°.

Oxides of Bismuth.

Bismuth monoxide, BiO, is prepared by heating basic bismuth oxalate,

$$(BiO)_2C_2O_4 = 2BiO + 2CO_2.$$

It is also formed as a black powder by the reduction of a tervalent bismuth compound by means of alkaline stannous solutions. It oxidises to the sesquioxide, Bi_2O_3, when heated in air and to a hydrated sesquioxide, $Bi_2O_3,2H_2O$, when moistened in contact with air; with acids it gives metallic bismuth and a tervalent salt.

Bismuth sesquioxide, Bi_2O_3, is found as a yellow powder under the name of BISMUTH OCHRE. It is formed on heating bismuth in air or oxygen, and can be prepared by igniting the oxide, hydroxide, carbonate, or nitrate. It is a heavy yellowish-white solid, and melts to a brown liquid; this glows when it crystallises at 820°, and undergoes a change of crystalline state (probably to the ordinary form of the oxide) with a further liberation of heat at 704°; a third and more stable modification which remains solid up to 860° can be obtained by roasting the ordinary form of the oxide. The sesquioxide dissolves in acids, but, unlike the corresponding oxides of arsenic and antimony, it does not possess any marked acid properties. **Bismuth hydroxide,** $Bi(OH)_3$, is obtained as a white amorphous precipitate by the action of ammonia or caustic alkali on a solution of a tervalent bismuth salt.

Higher Oxides of Bismuth.—Several higher oxides such as BiO_2, Bi_2O_5, and BiO_3, with and without combined water, have been prepared by the action of oxidising agents such as sodium hypochlorite upon tervalent bismuth compounds.

Bismuth Sulphides.

Bismuth monosulphide, BiS, has been prepared by the action of sulphuretted hydrogen on an alkaline solution of potassium bismuthyl

tartrate * (compare tartar emetic) in presence of stannous chloride. Hydrochloric acid converts it into a mixture of bismuth and the trichloride (compare the monoxide).

Bismuth sesquisulphide, Bi_2S_3, is found naturally as the mineral BISMUTHITE, which is isomorphous with stibnite, Sb_2S_3. It can be prepared artificially by the direct combination of bismuth and sulphur, or as a brownish-black precipitate by the action of sulphuretted hydrogen on acid solutions of the chloride. The precipitated sulphide is readily soluble in nitric acid and dissolves more slowly in boiling concentrated hydrochloric acid; unlike the sulphides of arsenic, antimony, and tin, it does not dissolve in alkalies, although it is soluble in solutions of potassium sulphide.

Higher sulphides of bismuth do not appear to be known.

Oxygen Salts of Bismuth.

Bismuth trinitrate, $Bi(NO_3)_3,5H_2O$, prepared by the action of nitric acid on the metal, is a soluble crystalline, deliquescent salt. The isomorphism of this nitrate with the nitrates of the rare earths, as well as of certain double nitrates of these elements, has been used as an aid to the fractionation of the rare earths (p. 668). The trinitrate is converted by the action of water into a **basic nitrate,** $Bi(OH)_2NO_3$, which is used extensively as a medicine in cases of diarrhœa, and as a means of following by means of *X*-rays the movements of food in the alimentary canal; for the last purpose it has, however, been superseded in part by barium sulphate.

Bismuth trisulphate, $Bi_2(SO_4)_3$, is obtained, like antimony trisulphate, by concentrating a solution of the metal or of its sulphide in strong sulphuric acid. By the action of water it gives a **basic sulphate,** $Bi_2O_3,SO_3,2H_2O$, and an anhydrous form of this, Bi_2O_3,SO_3 or $(BiO)_2SO_4$, is formed by heating the normal sulphate.

Bismuth phosphate, $BiPO_4$, and **bismuth arsenate,** $BiAsO_4$, are insoluble colourless compounds.

Bismuth also forms a series of **basic carbonates,** and the **orthosilicate,** $Bi_4(SiO_4)_3$, is found as a mineral.

Detection and Estimation of Bismuth.

A brittle metallic bead of bismuth is produced by heating its compounds on charcoal. Its solutions give, with sulphuretted hydrogen, a brownish-black precipitate of the sesquisulphide, Bi_2S_3; this differs from As_2S_3, Sb_2S_3, SnS, and SnS_2, in that it is insoluble in ammonium sulphide and in alkalies; it dissolves readily, however, in nitric acid. On dilution with water, basic salts are thrown down,

* Although bismuth does not form a stable compound of the type of tartar emetic, it can be retained in solution in presence of alkalies by means of tartaric acid, glycerine, or mannitol.

and ammonia gives a precipitate of the **hydroxide,** $Bi(OH)_3$, which does not dissolve in an excess of the reagent.

Bismuth is usually estimated by precipitating with ammonium carbonate, igniting, and weighing as the **sesquioxide**, Bi_2O_3. It can also be weighed in the metallic form after reduction with potassium cyanide.

The atomic weight of bismuth is based on determinations of the ratios $2Bi : Bi_2O_3$, $Bi_2O_3 : Bi_2(SO_4)_3$, and $BiBr_3 : 3AgBr$.

PART IV

THE METALS: TRANSITION SERIES

CHAPTER XXXVII

THE TRANSITION-ELEMENTS

	V	VI	VII	VIII			I	II	III
IV	23V	24Cr	25Mn	26Fe	27Co	28Ni	29Cu	30Zn	31Ga
V	41Cb	42Mo	43 —	44Ru	45Rh	46Pd	47Ag	48Cd	49In
VI	73Ta	74W	75 —	76Os	77Ir	78Pt	79Au	80Hg	81Tl
VII	91Pa	92U							

GENERAL CONSIDERATIONS.

Classification.

The first long period begins with a series of five elements closely resembling the first five elements of the two short periods, thus,

Short periods.

2. Helium	3. Lithium	4. Beryllium	5. Boron	6. Carbon
10. Neon	11. Sodium	12. Magnesium	13. Aluminium	14. Silicon.

Long period.

18. Argon	19. Potassium	20. Calcium	21. Scandium	22. Titanium

It closes with four elements which show a like similarity to the later members of the short periods, as follows:

Short periods.

6. Carbon	7. Nitrogen	8. Oxygen	9. Fluorine
14. Silicon	15. Phosphorus	16. Sulphur	17. Chlorine.

Long period.

32. Germanium	33. Arsenic	34. Selenium	35. Bromine.

The central portion of the period is, however, occupied by a series of nine TRANSITION-ELEMENTS for which no analogy is found in either of the short periods, namely,

23. Vanadium	24. Chromium	25. Manganese
26. Iron	27. Cobalt	28. Nickel
29. Copper	30. Zinc	31. Gallium.

These elements are heavy metals and with the single exception of gallium they are all commercially important. The principal element of the group is iron, and the first six elements, namely,

vanadium, *chromium*, *manganese*, *iron*, *cobalt*, and *nickel*,

are linked together by the fact that they are all metals of the same general type as iron and are all used extensively in making steel.

Series of elements corresponding with the nine transition-elements of period IV are found also in the second long period V and in the "very long period" VI which follows it (see the table at the head of this chapter); but these two series include only eight transition-elements each, since the two homologues of manganese are still unknown. Uranium, with the heaviest atom known, is (with the exception of protactinium, p. 733, which has not yet been isolated in quantity) a solitary representative of the transition-elements of period VII.

Characteristics of the Transition-elements.

(*a*) The transition-elements are marked by a very wide departure from the original "law of octaves." Thus, although the elements

23. Vanadium 24. Chromium 25. Manganese

and their homologues are placed for convenience in columns V, VI, VII of Table 61, under nitrogen, oxygen, and fluorine, they are totally different from the homologues of nitrogen, oxygen, and fluorine which occupy the alternate octaves. Again

29. Copper 30. Zinc 31. Gallium

are placed, for convenience, in columns I, II, and III, with the metals of the alkalies, of the alkaline earths, and of the earths, but differ widely from these metals, although they occupy precisely similar positions in the octaves.

(*b*) There is also an almost complete suppression in these elements of the "law of periodicity" as it appears in other parts of the table. Thus, the six typical steel-forming elements V, Cr, Mn, Fe, Co, Ni are clustered together as consecutive elements with increments of atomic weight amounting on the average to only 1·5 units, instead of the 16, 46, and 88 to 92 units postulated by Lothar Meyer as the normal increments for a series of closely-related elements in his original definition of periodicity (p. 545).

(*c*) This resemblance between elements forming a horizontal instead of a vertical series in the periodic table is most marked in the case of the elements which are placed in column VIII of the table, and lie at the bottom of the troughs of Lothar Meyer's atomic volume curve (Fig. 209, p. 546). For this reason, it is convenient, whilst retaining the vertical grouping for chromium and its homologues in column VI, the coinage metals in column I, the mercury group in column II, etc., to group the central elements into horizontal (instead of vertical)

triads, with iron, palladium, and platinum as the typical elements. These horizontal relationships are, however, not confined to these central triads, and Mendeléeff was so impressed by this fact that he actually showed the coinage metals, copper, silver, and gold, in two alternative positions in the table, namely, (i) with nickel, palladium, and platinum as additional elements in column VIII as well as (ii) in column I with the metals of the alkalies.

Physical Properties of the Transition-elements.

(*a*) *Density.*—The transition-elements, occupying the troughs of the atomic volume curve, are all heavy metals. Thus the nine transition-elements of period IV range in density from 6 to 9, the maximum being reached in the case of copper. In period V they reach a maximum at 12·5 in the case of rhodium. The highest known densities are found in the central triad of period VI, where a maximum value of 22·5 is recorded for osmium.

TABLE 80.—DENSITY OF THE TRANSITION-ELEMENTS.

IV	23V	24Cr	25Mn	26Fe	27Co	28Ni	29Cu	30Zn	31Ga
	6·0	6·9	7·4	7·86	8·8	8·8	**8·9**	7·1	5·9
V	41Cb	42Mo	43—	44Ru	45Rh	46Pd	47Ag	48Cd	49In
	12·7	9·0	—	12·0	**12·5**	12·1	10·5	8·6	7·2
VI	73Ta	74W	75—	76Os	77Ir	78Pt	79Au	80Hg	81Tl
	16·6	19·1	—	**22·5**	22·4	21·4	19·3	13·6	11·9

(*b*) *Melting-point.*—With the exception of the metals in the last two columns, the transition-elements are also characterised by high melting-points; but these attain a maximum value almost at the beginning of each series of nine elements and fall to very low values in the mercury and thallium groups. Thus, the six steel-forming elements, from vanadium to nickel, melt at temperatures ranging from 1720° to 1230°, the average being very near 1500°; there is then a steep descent to copper and zinc, and finally gallium (m.-p. 30°), the last transition-element of this series, is commonly obtained in a liquid condition. In period V the elements, molybdenum and ruthenium melt at about 2500°, but there is then a steep fall to rhodium, palladium, silver, cadmium, and indium (m.-p. 155°). In period VI the melting-points of the first four elements, Ta, W, Os, Ir, are very high, ranging from 2350° to 3060°, but platinum melts at 1755°, gold at 1063°, and mercury at — 39°.

TABLE 81.—MELTING-POINTS OF THE TRANSITION-ELEMENTS.

IV	23V	24Cr	25Mn	26Fe	27Co	28Ni	29Cu	30Zn	31Ga
	1720°	1615°	1230°	1530°	1480°	1452°	1083°	419°	30°
V	41Cb	42Mo	43—	44Ru	45Rh	46Pd	47Ag	48Cd	49In
	1950°	**2550°**	—	2450°	1950°	1549°	960°	321°	155°
VI	73Ta	74W	75—	76Os	77Ir	78Pt	79Au	80Hg	81Tl
	2900°	**3060°**	—	2700°	2350°	1755°	1063°	−39°	302°

(c) *Isomorphism.*—The transition-elements are characterised by very strongly marked isomorphism, especially amongst elements in the same horizontal series. Thus, silver forms a complete series of solid solutions with palladium, which immediately precedes it in the transition-series of period V, and a number of partial isomorphous series (compare copper and zinc, Fig. 278, p. 833) with cadmium, which follows it; it is also isomorphous with gold, which lies immediately below it in the periodic table, but forms an eutectic alloy with copper, which lies immediately above it. Gold forms a complete series of isomorphous mixtures with platinum and also with palladium, silver, and copper, but it gives eutectic alloys with nickel and with cobalt. Platinum forms complete isomorphous series with gold, and also with iron and copper, and two partial isomorphous series with silver. The isomorphism of the steel-forming elements is discussed in Chapter XLI below, but it is of interest to notice that whilst adjacent elements of this transition-series are always isomorphous, those which are separated by 3 (or sometimes 2 or 4) places give freezing-point curves which pass through a minimum, *e.g.*, V with Fe, Cr with Co or Ni, Mn with Co, Ni, or Cu.

Valency of the Transition-elements.

A conspicuous property of the transition-elements is the freedom which they appear to enjoy in the matter of valency, as contrasted with the comparatively rigid control of valency in the two short periods. It has been customary to assign to these elements the conventional valencies shown at the head of the following table, but the actual valencies diverge somewhat widely from these theoretical numbers, especially as regards the hypothetical oxides of the type RO_4, as may be proved by setting out the formulæ of the oxides of the nine transition-elements of period IV.

TABLE 82.—OXIDES OF THE TRANSITION-ELEMENTS.

Group.	V	VI	VII	VIII			I	II	III
Symbol of Element.	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
Hypothetical or Typical Oxides.	V_2O_5	CrO_3	Mn_2O_7	FeO_4	CoO_4	NiO_4	Cu_2O	ZnO	Ga_2O_3
Actual Oxides.									
Valency = 1	V_2O	—	—	—	—	—	**Cu_2O**	—	—
,, = 2	**VO**	**CrO**	**MnO**	**FeO**	**CoO**	**NiO**	**CuO**	**ZnO**	**GaO**
,, = 3	**V_2O_3**	**Cr_2O_3**	**Mn_2O_3**†	**Fe_2O_3**	**Co_2O_3**	**Ni_2O_3**	—	—	**Ga_2O_3**
,, = 4	VO_2	CrO_2*	MnO_2	—	—	—	—	—	—
,, = 5	**V_2O_5**	—	—	—	—	—	—	—	—
,, = 6	—	**CrO_3**	MnO_3	—	—	—	—	—	—
,, = 7	—	—	**Mn_2O_7**	—	—	—	—	—	—
,, = 2 & 3	—	—	Mn_3O_4†	Fe_3O_4	Co_3O_4	Ni_3O_4	—	—	—

* Chromous chromate, $Cr_2O_3 + CrO_3 = Cr_3O_6$ or $(CrO_2)_3$, valencies = 3 and 6.

† These compounds are perhaps manganous manganites, $2MnO,MnO_2 = Mn_3O_4$, and $MnO,MnO_2 = Mn_2O_3$, valencies 2 and 4.

These valencies may be interpreted most readily by recognising the existence of

(i) Typical valencies corresponding with the headings V, VI, VII . . . I, II, III, but with a total suppression, in the case of the elements of this series, of the valency indicated under the heading VIII by the hypothetical formula RO_4.

(ii) Steady valencies of 2 and 3 which appear to be characteristic of this group of transition-elements and which persist almost throughout the group.

These valencies, as indicated by the formulæ in heavy type in Table 82, cover nearly all the simple oxides of the transition-elements and all the most important series of salts.

TABLE 83.—PRINCIPAL VALENCIES OF THE TRANSITION-ELEMENTS.

V	VI	VII	VIII		
V 235	Cr 23–6	Mn 23467	Fe 23–	Co 23–	Ni 2– –
Cb –35	Mo 23–6	—	Ru 23467	Rh 234	Pd 2–4
Ta 2–5	W 2–46	—	Os 234	Ir 234	Pt 2–4

I	II	III
Cu 12–	Zn –2	Ga –23
Ag 1—	Cd –2	In 123
Au 1–3	Hg 12	Tl 1–3

In the two later periods the principal valencies of the transition-elements as set out in Table 83 are rather more complex. The homologues of vanadium and chromium follow these elements generally both in their higher and lower valencies. But the metals of the palladium and platinum triads add the valency 4 to those recorded for iron, cobalt, and nickel; and ruthenium (although its *X*-ray spectrum shows that it is not the missing element, Eka manganese, of atomic number 43) shows the same amazing range of valencies as manganese. The elements of the copper, zinc, and gallium groups show valencies of 1, 2, and 3 only; but these are distributed somewhat irregularly, the typical valency corresponding with the number at the head of each column being supplemented by univalency in Hg, In, Tl, bivalency in Cu, Ga, In, and tervalency in Au.

Variable Valency of the Transition-elements.

The chemical properties of the transition-elements are complex mainly on account of their variable valency. Thus, the general properties of iron in its bivalent ferrous salts correspond closely with those of magnesium, whilst in its tervalent ferric salts iron shows an even closer resemblance to aluminium. But the chemistry of iron differs from that of the alkaline earths of the magnesium group and of the earths of the aluminium group in virtue of the fact that iron can pass readily from the ferrous to the ferric state or conversely, in complete contrast with the fixed bivalency of the alkaline earths and the fixed tervalency of the earths. This change of valency plays an important part in the rusting of iron (p. 785), in which the metal dissolves in the

ferrous state and is precipitated again by oxidation to the ferric state; and in the same way, most of the important deposits of iron ore have been segregated by dissolution in the ferrous state, followed by reprecipitation in the ferric state.

This element of complexity is not distributed equally amongst the transition-elements. Thus in the first series of transition-elements the three elements,

23. *Vanadium,* 24. *Chromium,* 25. *Manganese,*

are particularly complex in their properties, since they exhibit not only the characteristic valencies 2 and 3 of the transition-group, but also the higher "typical valencies" of columns V, VI, and VII. The three central elements,

26. *Iron,* 27. *Cobalt,* 28. *Nickel,*

are much simpler in their properties, since most of their compounds exhibit only the transition-valencies 2 and 3, and nickel is almost exclusively bivalent. The last three elements,

29. *Copper,* 30. *Zinc,* 31. *Gallium,*

show equally simple properties, since the "typical valencies" 1, 2, and 3 of these elements either coincide with or suppress the "transition-valencies" 2 and 3, with the result that zinc, like nickel, is almost exclusively bivalent.

General Properties of the Iron Triad.

The central triad, namely,

26. *Iron,* 27. *Cobalt,* 28. *Nickel,*

exhibits in full the typical properties of the transition-elements. These may be summarised under three headings :—

(*a*) *Metals.*—The elements are metals of high melting-point, existing both in a magnetic (low temperature) form and in a non-magnetic (high temperature) form. In the latter form they are fully isomorphous with one another, and form complete series of solid solutions.

(*b*) *Formation of Salts.*—(i) The BIVALENT SALTS, *e.g.*, **ferrous chloride,** $FeCl_2$, are analogous to the bivalent salts of the alkaline earths, *e.g.*, magnesium chloride, $MgCl_2$. The bivalent oxides of these two metals are indeed constantly associated together in nature as isomorphous mixtures of silicates in minerals such as olivine, $[Mg,Fe]_2SiO_4$, and hornblende, $[Mg,Fe]SiO_3$. These bivalent salts are a dominant characteristic of the whole group of transition-elements; thus, SULPHATES of the type MSO_4, crystallising usually with 5 or 7 molecules of water, are formed by all the nine transition-elements from vanadium to gallium; and at least eight of these form isomorphous DOUBLE SULPHATES analogous to potassium magnesium sulphate, or schönite, which may be written as $K_2SO_4,MgSO_4,6H_2O$, or $K_2Mg(SO_4)_2,6H_2O$, or finally as $Mg(SO_4K)_2,6H_2O$, compare magnesium bicarbonate, $Mg(CO_3H)_2$, and the double carbonates such as $Mg(CO_3K)_2$.

(ii) The TERVALENT SALTS correspond in a similar manner with the tervalent salts of aluminium, with which element ferric iron is constantly associated in nature in minerals such as the felspars,

$K[Al,Fe]Si_3O_8$, and the spinels, $Mg[Al,Fe]_2O_4$. These tervalent salts are not quite so characteristic of the transition-elements as the bivalent salts, but are formed by six of the nine elements of this group, including five of the six steel-forming metals; the exceptions are limited to the triad of metals,

28. *Nickel*, 29. *Copper*, 30. *Zinc*,

which form only bivalent salts, except in the case of copper, which forms also a series of univalent cuprous salts. The tervalent sulphates, like the bivalent sulphates, form double salts with the sulphates of the alkalies, but these are of a different type and correspond with the alums such as $KAl(SO_4)_2,12H_2O$.

TABLE 84.—DOUBLE SULPHATES OF THE TRANSITION-ELEMENTS.

	Bivalent Sulphates.	*Tervalent Sulphates.*
Vanadium . . .	$K_2V''(SO_4)_2,6H_2O$	$KV'''(SO_4)_2,12H_2O$
Chromium . . .	$K_2Cr''(SO_4)_2,6H_2O$	$KCr'''(SO_4)_2,12H_2O$
Manganese. . .	$K_2Mn''(SO_4)_2,6H_2O$	$KMn'''(SO_4)_2,12H_2O$
Iron	$K_2Fe''(SO_4)_2,6H_2O$	$KFe'''(SO_4)_2,12H_2O$
Cobalt	$K_2Co''(SO_4)_2,6H_2O$	$KCo'''(SO_4)_2,12H_2O$
Nickel	$K_2Ni''(SO_4)_2,6H_2O$	—
Copper	$K_2Cu''(SO_4)_2,6H_2O$	—
Zinc	$K_2Zn''(SO_4)_2,6H_2O$	—
Gallium . . .	$Ga''SO_4,H_2O$	$KGa'''(SO_4)_2,12H_2O$

(iii) Iron, nickel, and cobalt also form mixed oxides of the type Fe_3O_4, in which one molecule of a bivalent oxide is combined with one molecule of the tervalent oxide, so that magnetic oxide of iron, Fe_3O_4, may be compared with the spinels, *e.g.*, $Mg''Al'''_2O_4$, and may be written $Fe''Fe'''_2O_4$.

(*c*) *Co-ordinated Compounds.*—These three elements also possess the remarkable property of forming CO-ORDINATED COMPOUNDS (see below, p. 797), in which *six* molecules or radicals are clustered round the metallic atom of a radical or ion in such a way that their ordinary chemical reactions are almost wholly concealed, as in the

FERROCYANIDES, *e.g.*,	$K_4Fe''C_6N_6$	or	$K_4[Fe.6CN]$
FERRICYANIDES, *e.g.*,	$K_3Fe'''C_6N_6$	or	$K_3[Fe.6CN]$
COBALTICYANIDES, *e.g.*,	$K_3Co'''C_6N_6$	or	$K_3[Co.6CN]$
COBALTINITRITES, *e.g.*,	$K_3Co'''(NO_2)_6$	or	$K_3[Co.6NO_2]$
COBALTAMMINES, *e.g.*,	$CoCl_3,6NH_3$	or	$[Co.6NH_3]Cl_3$.

These compounds show none of the simpler reactions by which ferrous, ferric, and cobaltic salts, cyanides, nitrites, and ammonia are commonly detected in solution; these disguised radicals are commonly distinguished, as in the formulæ set out above, by enclosing their symbols with that of the co-ordinating metal inside square brackets.

General Properties of Vanadium, Chromium, and Manganese.

These three elements, immediately preceding iron, cobalt, and nickel, and forming the earliest of the transition-elements, exhibit many of the typical properties of the group, as set out above for iron, nickel, and cobalt, thus:

(*a*) All three elements are *metals* of high melting-point, forming complete series of solid solutions with iron, although only manganese shows any signs of ferro-magnetism.

(*b*) *Bivalent and tervalent salts* predominate, but OXY-SALTS are also formed in which an oxide of the metal takes the place of the simple metallic radical, as in the

vanadyl chlorides Vo_2Cl, $VoCl$, $VoCl_2$, $VoCl_3$, and
vanadyl sulphates $Vo''SO_4$ and $K_2Vo''(SO_4)_2,6H_2O$,
$Vo'''_2(SO_4)_3$ and $KVo'''(SO_4)_2,12H_2O$,

where the VANADYL RADICAL VO (which is written above as Vo, compare Am and Cy) usually behaves as if it were a bivalent or tervalent metal, Vo″ or Vo‴, compare Fe″ and Fe‴.

(*c*) *Double cyanides* are formed by each member of the triad, and show all the properties of co-ordinated-compounds, *e.g.*,

Potassium vanadocyanide,	$K_4V''C_6N_6,3H_2O$.
Potassium vanadicyanide,	$K_3V'''C_6N_6$.
Potassium chromocyanide,	$K_4Cr''C_6N_6,2H_2O$.
Potassium chromicyanide,	$K_3Cr'''C_6N_6$.
Potassium manganocyanide,	$K_4Mn''C_6N_6,3H_2O$.
Potassium manganicyanide,	$K_3Mn'''C_6N_6$.

Chromium also forms a series of AMMINES, *e.g.*, $CrCl_3,5NH_3$ or $[Cr.5NH_3.Cl]Cl_2$, and $CrCl_3,6NH_3$ or $[Cr.6NH_3]Cl_3$ (p. 739), which are closely analogous to the cobaltammines referred to above.

(*d*) *Compounds of Higher Valency.*—Superposed on the normal characteristics of the transition-elements are a number of additional properties in which vanadium, chromium, and manganese, as the sixth, seventh, and eighth members of a long period, show some points of resemblance to the sixth, seventh, and eighth members of the short periods. These resemblances are surprising in view of the wide divergence of properties which exists between the non-metals N, O, F, and P, S, Cl, which terminate the two short periods, and the steel-forming metals V, Cr, Mn and their homologues, which replace them in the first octaves of the long periods; but it is precisely this twofold relationship, as analogues of the non-metals of the preceding octaves, and as members of the transition-group of metals, which gives to these elements and to their homologues their peculiarly complex chemical properties.

One point of analogy to the non-metals of similar valency has already been noticed in the "vanadyl" compounds, VOCl, etc., which may be com-

pared with "nitrosyl" compounds such as NOCl, "phosphoryl" compounds such as $POCl$, or with the "antimonyl" and "bismuthyl" compounds, SbOCl, BiOCl, etc., described in Chapter XXXVI; but it is the compounds of maximum valency, in which the analogy to the bivalent and tervalent elements of the central triad, Fe, Co, Ni, vanishes, which show the most striking resemblance to non-metallic compounds with a similar degree of oxidation, as set out in Table 85 below.

TABLE 85.—HIGHER OXIDES OF METALS AND NON-METALS.

	V	VI	VII
Elements	15. Phosphorus. 23. Vanadium.	16. Sulphur. 24. Chromium.	17. Chlorine. 25. Manganese.
Maximum Valency	5	6	7
Oxides	P_2O_5 V_2O_5	SO_3 CrO_3	Cl_2O_7 Mn_2O_7
Acids	HPO_3 HVO_3	H_2SO_4 H_2CrO_4	$HClO_4$ $HMnO_4$
Salts	$Na_3PO_4,12H_2O$ $Na_3VO_4,12H_2O$	K_2SO_4 K_2CrO_4	$KClO_4$ $KMnO_4$

The closeness of this analogy is shown in the complete isomorphism of

the VANADATES with the phosphates,
the CHROMATES with the sulphates, and
the PERMANGANATES with the perchlorates,

including the remarkable isomorphism of apatite, $Ca_5(PO_4)_3F$, with vanadinite $Pb_5(VO_4)_3Cl$, to which attention is directed below (p. 729).

General Properties of Copper, Zinc, and Gallium.

The physical properties of these three metals differ widely from those of the six steel-forming metals which precede them. Thus the melting-point falls nearly 400° from nickel to copper, more than 700° from copper to zinc, and nearly 400° from zinc to gallium, the melting-point of which is only 30°.

Their chemical properties are influenced on the one hand by the fact that they are "transition-elements," and on the other by analogies to elements equally distant from the *ends* of the preceding short periods. Thus the sixth, fifth, and fourth elements before chlorine are the univalent, bivalent, and tervalent metals of the alkalies, of the alkaline earths, and of the earths, and these valencies appear again in the triad now under consideration,

	I	II	III
Element	11. Sodium	12. Magnesium	13. Aluminium
Valency	1	2	3
Element	29. Copper	30. Zinc	31. Gallium
Valency	1 or 2	2	2 or 3

In the case of zinc, the valency thus imposed on the metal is identical with that which is most characteristic of the whole group of transition-elements, and none but bivalent compounds are formed. In the case of gallium, the tervalency of aluminium agrees with one of the normal valencies of the transition-elements (as in the ferric salts)

and therefore becomes the principal valency of gallium; but the dominant bivalency of the transition-elements is retained in the gallous salts, *e.g.*, $GaSO_4$ and $GaCl_2$. In the case of copper, the bivalent cupric salts show the predominant valency of the transition-elements; but the univalency of sodium finds a parallel in a series of univalent cuprous salts, just as the higher valencies of phosphorus, sulphur, and chlorine are reflected in the higher oxides of vanadium, chromium, and manganese.

CHAPTER XXXVIII

VANADIUM AND ITS HOMOLOGUES

Atomic number.	*Element.*	*Symbol.*		*Atomic weight.*
23	Vanadium	V	=	51·0
41	Columbium	Cb*	=	93·5
73	Tantalum	Ta	=	181·5
91	Protactinium	Pa	=	230 (?)

Occurrence of Vanadium.

Vanadium is found in igneous rocks to the extent of about 0·025 per cent. V_2O_3 (compare NiO, 0·025 per cent.) as contrasted with 0·3 per cent. of P_2O_5. Its most important ore is VANADINITE, $Pb_5(VO_4)_3Cl$, a compound analogous to apatite, $Ca_5(PO_4)_3F$, but containing lead in place of calcium, chlorine in place of fluorine, and vanadium in place of phosphorus. CARNOTITE, a potassium uranyl vanadate, $K(UO_2)VO_4,1\frac{1}{2}H_2O$, is also an important ore of these two elements.

Metallic Vanadium.

(*a*) *Preparation.*—Metallic vanadium has been prepared in small quantities by reducing the anhydrous dichloride in very pure dry hydrogen,

$$VCl_2 + H_2 = V + 2HCl.$$

Crude vanadium can be prepared by reducing vanadic oxide with aluminium,

$$V_2O_3 + 2Al = 2V + Al_2O_3;$$

a more complete reduction, giving a much purer product, is obtained when the pentoxide, V_2O_5, is reduced by heating with the mixed metals of the rare earths (p. 668).

(*b*) *Physical Properties.*—Vanadium is a silver-white metal, harder than steel or quartz. Its density is about 6, and is the lowest of the group of steel-forming metals which extends from vanadium to nickel; its melting-point (1720°), on the other hand, is the highest of the

* Or Niobium, Nb.

series, and is almost equal to that of platinum (1755°). The metal is isomorphous with γ-iron (p. 770) and has a valuable effect in increasing the tensile strength of steel without diminishing its ductility; vanadium steels are therefore used where great strength is required without excessive weight; they are also of special value on account of their resistance to "fatigue," *i.e.*, they do not become brittle or weak when subjected to incessant alterations of stress, *e.g.*, in springs.

(*c*) *Chemical Properties.*—Metallic vanadium is stable in the air and is not oxidised by cold water, but the powder burns brilliantly (like iron) in a flame, or when heated in oxygen. Like silicon, it is very resistant to the action of acids, but it is dissolved by hydrofluoric acid and by oxidising agents such as nitric acid, chloric and perchloric acids, and ammonium persulphate; it is also dissolved by molten sodium hydroxide, although the alkali does not attack it in solution.

An interesting point in the history of vanadium is the fact that Berzelius mistook the vanadyl salts VOX for salts of a metal analogous to chromium, the metal described by Berzelius being either an oxide or a nitride, VN, according to the method used in its preparation; this error was corrected by Roscoe in 1867.

(*d*) *Valency.*—Vanadium exhibits a wide range of valencies, but in the most important compounds the valency is 2, 3, or 5.

Chlorides, VCl_2, VCl_3, VCl_4.
Oxy-chlorides, $(VO)_2Cl$, $VOCl$, $VOCl_2$, $VOCl_3$.
Oxides, V_2O, VO, V_2O_3, VO_2, V_2O_5.
Sulphides, VS, V_2S_3, V_2S_5.

Sulphates:

(i)	$V''SO_4,7H_2O$,	compare $Fe''SO_4,7H_2O$.
	$(NH_4)_2SO_4,V''SO_4,6H_2O$,	compare $(NH_4)_2SO_4,Fe''SO_4,6H_2O$.
(ii)	$V'''_2(SO_4)_3$,	compare $Cr'''_2(SO_4)_3$.
	$NH_4V'''(SO_4)_2,12H_2O$,	compare $NH_4Al'''(SO_4)_2,12H_2O$.
(iii)	$VOSO_4$,	compare $Cr''SO_4$.
	$(VO)_2(SO_4)_3$,	compare $Cr'''_2(SO_4)_3$.
	$KVO(SO_4)_2$,	compare $KCr'''(SO_4)_2$.

Nitrides, VN, VN_2.
Silicides, V_2Si, VSi_2.

Vanadic Acid and the Vanadates.

Vanadium is usually found in the form of VANADATES as the acid constituent of the mineral. Vanadic acid is separated by extracting the ores with strong hydrochloric acid; on evaporating the solution with ammonium chloride, **ammonium metavanadate**, NH_4VO_3, crystallises out, since it is only sparingly soluble in presence of ammonium chloride.

Orthovanadic acid, H_3VO_4, is not known, but some of its salts are found as minerals, *e.g.*, vanadinite, $Pb_5(VO_4)_3Cl$, and mottramite, $[Cu,Pb]_5(VO_4)_2(OH)_4$, also $BiVO_4$ and $Cu_3(VO_4)_2,H_2O$; other orthovanadates have been prepared

artificially. Salts containing two, four, and six atoms of vanadium have also been prepared and analysed.

Metavanadic acid, HVO_3, is prepared by eliminating ammonia from the ammonium salt, *e.g.*, by warming it with ammonium chloride and copper sulphate, which probably combines with the ammonia to form a cuprammonium compound (p. 841); the acid is used as a yellow pigment under the name of VANADIUM BRONZE. The **lead salt,** $Pb(VO_3)_2$, is found as a mineral.

Vanadic anhydride, V_2O_5, is prepared by igniting the ammonium salt. A solution of this oxide in sulphuric acid shows a very remarkable series of colour changes when reduced progressively to the monoxide, VO.

Vanadium Monoxide and the Vanadyl Compounds.

Vanadyl chloride, $VOCl_3$, is prepared by heating vanadic anhydride with carbon in a current of chlorine,

$$V_2O_5 + 3C + 3Cl_2 = 2VOCl_3 + 3CO;$$

compare $$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO.$$

It is a lemon-yellow liquid boiling at 127° (compare $POCl_3$, b.-p. 108°).

Vanadyl sesquisulphate, $(VO)_2(SO_4)_3$, is formed by dissolving the pentoxide in fairly strong sulphuric acid,

$$V_2O_5 + 3H_2SO_4 = (VO)_2(SO_4)_3 + 3H_2O;$$

compare $$Al_2O_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O;$$

whilst potassium vanadate with strong sulphuric acid gives a **potassium vanadyl sulphate,** $KVO(SO_4)_2$, corresponding with an anhydrous alum.

Vanadious oxide, VO, which plays the part of a metal in the vanadyl salts, can be prepared by reducing the higher oxides with potassium, or from vanadyl trichloride, $VOCl_3$, by reduction with hydrogen in presence of red-hot charcoal. It is a grey powder possessing both metallic lustre and metallic conductivity, and was regarded by Berzelius as a metal resembling chromium.

When heated in chlorine the monoxide is reconverted into **vanadyl trichloride,** $VOCl_3$. Heating with zinc at 400° converts this into **vanadyl dichloride,** $VOCl_2$, forming green deliquescent crystals, whilst reduction with hydrogen in a red-hot tube gives also **vanadyl monochloride,** VOCl. The monochloride may be regarded as a salt of the **sesquioxide,** V_2O_3, or $(VO)_2O$, which is formed when the monoxide is burnt in air.

Chemical Relationships of Vanadium.

(*a*) As an element, vanadium resembles the steel-forming metals chromium, manganese, cobalt, and nickel in forming a complete series of solid solutions with iron. It also resembles these elements in forming bivalent and tervalent salts, as well as vanadocyanides and vanadicyanides, *e.g.*, $K_4V''C_6N_6$ and $K_3V'''C_6N_6$; compare $K_4Fe''C_6N_6$ and $K_3Fe'''C_6N_6$.

(*b*) In its quinquevalent compounds vanadium shows a distinct analogy to phosphorus, the most striking illustration of which is found

in the isomorphism of vanadinite, $Pb_5(VO_4)_3Cl$, with apatite, $Ca_5(PO_4)_3F$. The isomorphism of the vanadates with the phosphates corresponds exactly with the isomorphism of the chromates with the sulphates and of the permanganates with the perchlorates. The univalent and tervalent vanadyl compounds also bring vanadium into line with phosphorus, antimony, and bismuth.

(c) Whilst the steely character of the element links it with the metals which follow it in a *horizontal* series, and the isomorphism of its quinquevalent compounds links it with phosphorus and arsenic in the same *vertical* column of the periodic table, there is also some justification for tracing a resemblance along a *diagonal* line in the table running from boron through silicon to vanadium. Thus, the readiness of the element to unite both with oxygen and with nitrogen, and the great stability of its nitride, VN, correspond closely with the properties of boron, the tervalency of which enables it also to form a very stable nitride, BN, of simple formula. The tendency of the vanadic acids to form complex salts containing up to six atoms of vanadium is also in harmony with the properties of silicon and boron, in spite of the fact that the vanadates are derived from a quinquevalent oxide, the silicates from a quadrivalent oxide, and the borates from a tervalent oxide. The diagonal relationship thus indicated may be continued through vanadium to molybdenum (p. 746), which also exhibits many of the characteristics to which attention is here directed.

41. **Columbium**, Cb = 93·5, and 73. **Tantalum**, Ta = 181·5.

(a) *Occurrence*.—These two elements are far less abundant even than vanadium, which they resemble in their acid-forming properties. The principal minerals in which they occur are COLUMBITE, a **ferrous columbate,** $FeCb_2O_6$ (compare HVO_3 and HPO_3), in which a part of the ferrous iron may be replaced by manganese, and a part of the columbium by tantalum. TANTALITE is essentially a **ferrous tantalate,** $FeTa_2O_6$, containing some manganese in the place of iron and often a considerable proportion of columbium in place of tantalum. These two minerals form black opaque crystals belonging to the orthorhombic system of a submetallic lustre and of high density (density of columbite = 5·5).

(b) *Metals*.—Columbium (or niobium) and tantalum are metals with a steely lustre, which show many points of resemblance to vanadium, although their melting-points and densities are considerably higher :

Melting-points .	V = 1720°	Cb = 1950°	Ta = 2900°
Densities . . .	V = 6	Cb = 12·7	Ta = 16·6.

Both metals are capable of being rolled into foil or drawn into wire, and tantalum wires have been used (like tungsten, the next element in the periodic classification) for the filaments of incandescent lamps; these filaments have a very high tensile strength, about 60 tons

per square inch, although this is much inferior to that of tungsten filaments (p. 748). It is noteworthy that, as in the case of vanadium, the oxide, CbO, and the nitride, TaN, were at first mistaken for metals, and the salts containing the oxidised radicals, CbO and TaO, were at first regarded as salts of the simple metals.

(c) *Valency and Derivatives.*—Columbium forms a *tervalent* and a *quinquevalent* chloride,

$$CbCl_3 \text{ and } CbCl_5,$$

and also a series of oxy-derivatives, including

$$CbOF_3,\ CbOCl_3,\ CbOBr_3, \text{ and } CbOS_3.$$

Tantalum forms *bivalent* and *quinquevalent* halogen derivatives, such as

$$TaCl_2,\ TaCl_5,\ TaBr_5,$$

but oxy-derivatives analogous to the vanadyl salts are almost unknown. Both elements form nitrides, CbN, TaN, of the type of boron nitride, BN.

(d) *Columbates and Tantalates.*—The most important compounds of these two elements are the COLUMBATES and TANTALATES, derived from **columbic acid,** $HCbO_3$, and **tantalic acid,** $HTaO_3$, or from more complex acids of the same valency, Two of these compounds have already been described as ores of columbium and tantalum.

(e) *Fluorides and Oxyfluorides.*—When a mixture of columbic anhydride, Cb_2O_5, and fluorspar is ignited in a current of hydrochloric acid, **columbyl trifluoride,** $CbOF_3$, sublimes in small crystals; it can be purified by recrystallisation from water and used to prepare **columbium pentoxide,** Cb_2O_5, by decomposing it with sulphuric acid and boiling the solution with water; reduction with metallic sodium converts it into **columbium monoxide,** CbO. A point of special interest in connection with columbyl fluoride is the existence of an isomorphous series of **double fluorides,** including

Potassium titanifluoride,	$2KF,TiF_4$	or	K_2TiF_6,
Potassium columbyl fluoride,	$2KF,CbOF_3$	or	K_2CbOF_5,
Potassium tungstyl fluoride,	$2KF,WO_2F_2$	or	$K_2WO_2F_4$,

in which there is an isomorphous replacement of univalent fluorine by bivalent oxygen. By the action of hydrofluoric acid the columbyl salt is converted into **potassium columbifluoride,** K_2CbF_7.

Tantalum does not appear to form a simple oxyfluoride, but **potassium tantalifluoride,** K_2TaF_7, is an extremely stable salt which does not decompose even at a white heat, and is the compound by means of which tantalum is separated from its ores.

91. **Protactinium,** Pa = 230 (?), is a radioactive element of which traces have been separated from pitchblende in association with tantalum (see p. 903).

CHAPTER XXXIX

CHROMIUM AND ITS HOMOLOGUES

Atomic number.	*Element.*	*Symbol.*		*Atomic weight.*
24	Chromium	Cr	=	52·0
42	Molybdenum	Mo	=	96·0
74	Tungsten*	W	=	184·0
92	Uranium	U	=	238·2

Classification and Properties.

(*a*) The relationship of **chromium** to the transition-elements of the *iron* group has already been discussed (p. 726). **Molybdenum** and **tungsten** (following niobium and tantalum respectively in the periodic table) may be regarded as members of two transition-groups of higher atomic weight in which *palladium* and *platinum* are the typical metals; they are, however, separated from the palladium and platinum triads by two missing elements, the unknown homologues of manganese. **Uranium,** the element of highest atomic weight, is perhaps a representative of another group of transition-elements, but this group is at present purely hypothetical.

(*b*) The *physical properties* of the group are as follows :—

TABLE 86.—PROPERTIES OF THE CHROMIUM GROUP OF METALS.

	Density.	*Melting-point.*
Chromium	6·9	1615°
Molybdenum	9·0	2550°
Tungsten	19·1	3060°
Uranium	18·7	about 1800°

The metals are all of the "steel" type, and molybdenum and tungsten, as well as chromium, are important constituents of special steels. Their high melting-points are also noteworthy, that of tungsten being higher than in the case of any other metal.

(*c*) In their *chemical properties* they show the same wide range of valencies and diversity of types of compounds that have been noted

* Or Wolfram.

in vanadium and its homologues. Conspicuous amongst the chemical properties of the group are

(i) The acid character of the higher oxides, which form important series of CHROMATES, MOLYBDATES, and TUNGSTATES. Except in the case of chromium, where the tervalent chromic salts, *e.g.*, chrome alum, $KCr'''(SO_4)_2,12H_2O$, and the chromites, *e.g.*, $FeCr'''_2O_4$, are important, these acidic oxides and their salts dominate the chemistry of the group, and give rise to the remarkable feature of metals which are familiar in the laboratory mainly as the acid-component of salts, such as lead chromate, $PbCrO_4$, potassium dichromate, $K_2Cr_2O_7$, ammonium molybdate, $(NH_4)_2MoO_4$, sodium tungstate, Na_2WO_4, etc.

(ii) This group of metals also shares with vanadium and its homologues a strong tendency to form salts in which a metallic oxide plays the part of a metal. This phenomenon brings these elements into relationship with non-metals of similar valency; thus CrO_2Cl_2, MoO_2F_2, WO_2F_2 may be compared with SO_2Cl_2, just as VOCl and $CbOF_3$ may be compared with NOCl, $POCl_3$, etc. In the case of uranium, even the common oxy-salts of the metal are of this type, *e.g.*, uranyl nitrate, $UO_2(NO_3)_2$, uranyl sulphate, $(UO_2)SO_4$, etc., and the complete removal of oxygen from the metal is only less difficult than in the case of vanadium.

24. CHROMIUM. Cr = 52·0.

Occurrence of Chromium.

Chromium is not found in the free state, but is present to the extent of about 0·05 per cent. in igneous rocks, where chromic oxide, Cr_2O_3, may replace alumina, Al_2O_3, both in aluminates such as spinel, $MgAl_2O_4$, and in alumino-silicates such as garnet, $Ca_3Al_2(SiO_4)_3$. It is segregated, mainly in subsilicic rocks, as **ferrous chromite,** $Fe(Cr_2O_4)$, in the form of CHROMITE or CHROME IRONSTONE, a cubic mineral of the spinel group, isomorphous with magnetite, Fe_3O_4. **Lead chromate,** $PbCrO_4$, is also found, as CROCOITE, a red mineral which gives an orange-yellow streak and is identical in composition with "chrome yellow."

Metallic Chromium.

(*a*) *Preparation.*—The most convenient method of preparing chromium is by reducing the oxide with aluminium (p. 657),

$$\underset{268,000}{Cr_2O_3} + 2Al = 2Cr + \underset{380,000}{Al_2O_3} + 112,000 \text{ calories};$$

as in the case of thermite, the reduction is not easy to start, but proceeds with great evolution of heat.

On a larger scale, chromic oxide may be reduced by carbon in an electric furnace,

$$Cr_2O_3 + 3C = 2Cr + 3CO;$$

the product is freed from carbide (as in the case of iron) by remelting the crude metal with the oxide. Alloys of iron and chromium, known as FERRO-CHROME, are also prepared by reducing chrome-ironstone with carbon in an electric furnace,

$$FeCr_2O_4 + 4C = Fe + 2Cr + 4CO.$$

(*b*) *Physical Properties.*—In its general properties metallic chromium resembles iron. Its melting-point, 1615°, is higher than that of iron, whilst its boiling-point, 2200°, is distinctly lower; its density, 6·9, is below that of iron.

(*c*) *Alloys.*—Chromium is isomorphous with nickel (Fig. 273, p. 804) and with cobalt, but each series of solid solutions includes an alloy of minimum melting-point. Chromium, when melted, forms two liquid layers with copper, and is also immiscible with the fusible metals zinc, lead, cadmium, bismuth, and tin; in this respect it resembles the tervalent metal aluminium (p. 525)

Metallic chromium is a constituent of NICHROME, a nickel-chromium alloy of high melting-point (*e.g.* Ni 60, Fe 25, Cr 15 per cent.), which is used in the form of wire for winding the resistances of small electric furnaces,

(i) because it does not oxidise when heated in air,
(ii) because it has a high resistance,
(iii) because the lowest melting-point of the series of alloys is about 1300°.

Alloys of iron with about 12 per cent. of chromium and 0·3 per cent. of carbon are used under the name of STAINLESS STEEL, because, whilst possessing the mechanical qualities that are necessary for cutlery, they also have the property of resisting in a marked degree the attack of acids, including the action of air and water, which gives rise to the rusting of metallic iron

Chromium and tungsten are also essential constituents of HIGH SPEED STEELS (p. 777), which have the property of retaining their hardness even at a red heat, so that a cutting tool of this material can do something like one hundred times as much work as a carbon-steel without softening and losing its edge.

Chemical Properties of Chromium.

(*a*) *General.*—Chromium has a greater affinity for oxygen than iron; it is therefore less easily prepared from its oxide and, conversely, the metal burns more brightly than iron when heated in the oxy-hydrogen flame. It dissolves rapidly in dilute acids, liberating hydrogen, but like aluminium it does not dissolve in concentrated nitric acid;

it also becomes " passive " towards dilute acids after being dipped in a solution of chromic acid.

(*b*) *Valency*.—Chromium forms

(i) Bivalent CHROMOUS SALTS, such as **chromous chloride,** $CrCl_2$, which are bright blue in colour;

(ii) Tervalent CHROMIC SALTS, such as **chromic chloride,** $CrCl_3$, which are violet or green, and CHROMITES, in which the tervalent oxide acts as the acid constituent of the salt;

(iii) Sexavalent compounds, including CHROMIC ANHYDRIDE, CrO_3, and the CHROMATES and DICHROMATES derived from it;

(iv) PERCHROMIC ACID and PERCHROMATES, in which the metal is still more highly oxidised.

(*c*) *Uses*.—On account of their colour, the green chromic oxide and yellow and red chromates are used extensively as pigments.

Chromic acid and its derivatives, which part somewhat readily with their oxygen, are used as oxidising agents in organic and inorganic chemistry.

Chromium salts are used as a source of chromium hydroxide in tanning, chrome-tanned leather being very resistant to water and to oils, and in dyeing, where the hydroxide acts as a MORDANT (compare $Al(OH)_3$, p. 662) for fixing dyestuffs on to the fibre.

Bivalent Derivatives of Chromium.

The CHROMOUS SALTS, which are usually prepared by reduction from the chromic salts, are analogous to the ferrous salts (p. 784). They are, however, far more powerful reducing agents; thus, the hydroxide liberates hydrogen when heated and the carbonate decomposes water and liberates hydrogen at 100° (compare potassium cobaltocyanide, p. 800).

Chromous chloride, $CrCl_2$, is obtained by heating chromium in hydrogen chloride gas (compare stannous chloride, $SnCl_2$, and ferrous chloride, $FeCl_2$) or by reducing chromic chloride, $CrCl_3$, in a current of hydrogen. A sky-blue solution of chromous chloride can be prepared by reducing a chromate or a chromic salt by means of zinc and hydrochloric acid. By pouring the crude product of reduction into a saturated solution of sodium acetate, **chromous acetate,** $Cr(C_2H_3O_2)_2$, can be precipitated; on redissolving the acetate in hydrochloric acid and crystallising out in the absence of air, the **tetrahydrate,** $CrCl_2,4H_2O$, separates in blue needles. The vapour density of the anhydrous chloride is intermediate between those required for the formulæ $CrCl_2$ and Cr_2Cl_4.

Chromous sulphate, $CrSO_4$, prepared by dissolving metallic chromium or chromous acetate in dilute sulphuric acid, separates from water in blue crystals as the **heptahydrate,** $CrSO_4,7H_2O$, isomorphous with ferrous sulphate; it forms a blue **double-sulphate,**

$K_2SO_4,CrSO_4,6H_2O$, corresponding with the double sulphates of copper, zinc, manganese, etc.

Chromous hydroxide, $Cr(OH)_2$, precipitated by the action of potassium hydroxide on chromous chloride, is a brownish-yellow compound, which oxidises readily, and when heated decomposes according to the equation

$$2Cr(OH)_2 = Cr_2O_3 + H_2O + H_2.$$

Chromous carbonate, $CrCO_3$, prepared by precipitation from a solution of the chloride, is a yellow or reddish-brown compound which forms double salts with the alkaline carbonates (compare magnesium, p. 619, and copper, p. 841).

CHROMIC OXIDE, CHROMITES, AND CHROMIC SALTS.

Chromic Oxide and Hydroxide.

Chromium sesquioxide, Cr_2O_3, is the most stable of the oxides of chromium and is the form in which (in combination with other oxides) chromium is most commonly found in nature. It is formed by the oxidation of the metal, by ignition of the hydroxide, or by decomposition of the higher oxide, CrO_3. It is also produced by igniting mercurous chromate or ammonium dichromate,

$$4Hg_2CrO_4 = 2Cr_2O_3 + 8Hg + 5O_2,$$
$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4H_2O.$$

It is prepared commercially by reducing potassium dichromate, *e.g.*, by boiling it with sulphur, by igniting it in a crucible with sulphur, or by igniting it with ammonium chloride and sodium carbonate:

$$K_2Cr_2O_7 + S = Cr_2O_3 + K_2SO_4,$$
$$K_2Cr_2O_7 + 2NH_4Cl = Cr_2O_3 + 2KCl + N_2 + 4H_2O.$$

The oxide is obtained as a green powder, and is used as a pigment under the name of CHROME GREEN. It melts at a white heat, and on cooling forms crystals which are isomorphous with corundum or emery, Al_2O_3, and are equally hard. The oxide is extremely stable and, unlike ferric oxide, is not reduced by hydrogen or carbon monoxide; the metal can, however, be prepared by heating the oxide with carbon at 1200°. A **hydrated oxide,** $Cr_2O_3,2H_2O$, prepared by the action of boiling water on a crude chromium borate (made by heating together potassium dichromate and boric acid), is also used as a pigment under the name of EMERALD GREEN.

Chromic hydroxide, $Cr(OH)_3$, is a very weak base, since it is precipitated (with ferric and aluminium hydroxides) by ammonia in presence of ammonium chloride,

$$CrCl_3 + 3NH_4OH = Cr(OH)_3 + 3NH_4Cl.$$

Moreover, the **sesquisulphide,** Cr_2S_3, which can be prepared by direct combination of chromium with sulphur, or by igniting the oxide in sulphuretted hydrogen, is decomposed by water; ammonium sulphide

therefore precipitates the hydroxide and not the sulphide from solution,

$$CrCl_3 + 3NH_4HS + 3H_2O = Cr(OH)_3 + 3NH_4Cl + 3H_2S.$$

The hydroxide also shows weak acid properties, since it dissolves in an excess of caustic alkali, forming a CHROMITE (see below).

Chromites.

Potassium chromite, $KCrO_2$, is probably formed when chromic hydroxide is precipitated from solution and redissolved in an excess of potassium hydroxide; but the compound is unstable and is decomposed by boiling or by partial neutralisation; in this respect the behaviour of chromic oxide is intermediate between that of alumina and ferric oxide. Stable crystalline CHROMITES, such as $FeCr_2O_4$, $MnCr_2O_4$, $ZnCr_2O_4$, are, however, found as minerals, or can be prepared artificially by melting the oxides together, *e.g.*, with boric oxide as a flux. The most important of these is **ferrous chromite,** $FeCr_2O_4$, which, in the form of CHROME IRON ORE or CHROMITE, is the principal source from which chromium compounds are derived. This compound crystallises in the cubic system and is isomorphous with the spinels, *e.g.*, $MgAl_2O_4$, and with magnetite, Fe_3O_4, or $Fe(Fe_2O_4)$; chromite therefore always contains magnesia and sometimes manganous oxide, replacing ferrous oxide, whilst alumina and ferric oxide may replace some of the chromic oxide. Chromite is a very stable compound and separates at an early stage from the magma in ferromagnesian rocks; it has indeed been suggested that deposits of chrome iron ore have been formed by segregation under gravity of crystals which have separated directly from the liquid magma. The chromium is usually separated from chromite by oxidation to potassium dichromate, and chromic salts are prepared by reduction from the dichromate.

Soluble Chromic Salts.

Chromic chloride, $CrCl_3$, can be prepared in the same way as aluminium chloride, $AlCl_3$, by the combined action of chlorine and carbon on the sesquioxide,

$$3Cl_2 + Cr_2O_3 + 3C = 2CrCl_3 + 3CO.$$

It forms pale violet scales which vaporise above 1000°, the vapour density agreeing satisfactorily with that required for the formula $CrCl_3$. Anhydrous chromic chloride combines with ammonia to form a **hexammine,** $CrCl_3,6NH_3$, from which all the chlorine can be precipitated by silver nitrate, and a **pentammine,** $CrCl_3,5NH_3$, from which only two-thirds of the chlorine can be precipitated. This difference is expressed (pp. 725 and 797) by writing the formulæ thus:

$$[Cr.6NH_3]Cl_3 \quad \text{and} \quad [Cr.5NH_3.Cl]Cl_2,$$

where the chlorine and ammonia which cannot be detected by the ordinary tests of qualitative analysis are shown inside the brackets.

whilst the chlorine shown outside the brackets can be precipitated in the usual way by silver nitrate.

A similar difference appears to exist between the **green hexahydrate,** $CrCl_3,6H_2O$, which is precipitated by hydrogen chloride from a cold saturated solution of the salt, and from which only one-third of the chlorine is precipitated by silver nitrate, and the **violet hexahydrate,** which is obtained (in grey crystals giving a violet solution in water) when the precipitation is carried out after warming the solution to 80° and cooling to 0°, and which gives up all its chlorine to silver nitrate. This difference is expressed by writing the formulæ thus :

$[Cr.6H_2O]Cl_3$	$[Cr.4H_2O.Cl_2]Cl,2H_2O.$
Violet hexahydrate	Green hexahydrate

The violet and the green forms of the salt can exist independently in solution, the two forms being converted into one another only gradually. Dilute solutions of the chloride are normally violet in colour, whilst concentrated or acid solutions are green, but the change of colour is not instantaneous and may occupy some hours. It is stated that the violet anhydrous chloride only dissolves in water when a trace of a reducing agent ($CrCl_2$, $SnCl_2$, $FeCl_2$, etc.) is present, which acts as a catalytic agent to convert the violet into the green form of the salt.

Chromic sulphate, $Cr_2(SO_4)_3,18H_2O$, compare $Al_2(SO_4)_3,18H_2O$.—This salt can be prepared in violet octahedra by covering chromium hydroxide with cold concentrated sulphuric acid, dissolving in water the crude crystals which separate from the acid, and reprecipitating them by the addition of alcohol. The sulphate is, however, more commonly prepared in the form of an alum ; thus, **potassium chromic sulphate** or CHROME ALUM, $KCr(SO_4)_2,12H_2O$, can be prepared very readily by reducing potassium dichromate with sulphur dioxide,

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = 2KCr(SO_4)_2 + H_2O.$$

It is also obtained as a by-product of the reduction of potassium dichromate in presence of sulphuric acid in the dichromate battery (p. 196) (where it is used as a depolariser to oxidise hydrogen), as well as in other cases where a mixture of potassium dichromate and sulphuric acid is used as an oxidising agent. Chrome alum crystallises in deep purple octahedra, and is completely isomorphous with the corresponding aluminium salt ; it forms a purple solution, which becomes dark green when heated to 70°, but returns slowly to its original colour.

By heating the *violet* sulphate, $Cr_2(SO_4)_3,18H_2O$, until it has the composition $Cr_2(SO_4)_3,8H_2O$, a *green* sulphate is obtained which differs from the violet salt in that it is soluble in alcohol, does not crystallise on evaporation, and does not give the reactions either of chromium or of a sulphate, although it reverts gradually to the ordinary violet form in solution. A *green* sulphate, $Cr_2(SO_4)_3,6H_2O$, with similar properties, has also been prepared by reducing chromic acid, CrO_3, with sulphur dioxide below 0°. An intermediate product, in which only one-third of the sulphuric acid can be precipitated, is obtained when the violet sulphate is turned green by heating to 100°, or merely by boiling the solution. These changes of colour are evidently similar in origin

to those observed in chromic chloride, and are expressed by writing the green sulphate as $[Cr.1\frac{1}{2}SO_4\,3H_2O]$, where the $1\frac{1}{2}SO_4$ are equivalent to three univalent radicals, making, with $3H_2O$, the usual total of six radicals inside the brackets.

CHROMIC ACID AND ITS DERIVATIVES.

Chromic Acid and the Chromates.

Chromium trioxide, CrO_3, is analogous to sulphur trioxide, SO_3, and forms a series of CHROMATES which are analogous to, and usually isomorphous with, the corresponding sulphates, *e.g.*,

	$Na_2CrO_4,10H_2O$	K_2CrO_4	$BaCrO_4$	$PbCrO_4$;
compare	$Na_2SO_4,10H_2O$	K_2SO_4	$BaSO_4$	$PbSO_4$.

Lead chromate is found as a mineral and the insoluble lead and barium chromates are used as pigments. In addition to these compounds there is a well-known series of DICHROMATES, *e.g.*, potassium dichromate, $K_2Cr_2O_7$, which are analogous to the pyrosulphates, *e.g.*, $K_2S_2O_7$, but differ from them in being more stable than the normal salts and capable of being crystallised unchanged from water. Chromium trioxide also differs from sulphur trioxide in that, although very soluble in water, it has no marked affinity for it and commonly separates from solution in an anhydrous form.

Chromic Acid.

Chromic anhydride or **chromium trioxide,** CrO_3, is prepared by adding concentrated sulphuric acid to a cold saturated solution of potassium chromate,

$$K_2CrO_4 + H_2SO_4 = K_2SO_4 + CrO_3 + H_2O.$$

It separates in crimson needles, which are contaminated with sulphuric acid. This can be removed by evaporation after melting the crystals, or by washing with nitric acid, which can then be evaporated without melting the crystals ; or the crystals may be drained and recrystallised from water after adding barium chromate to precipitate sulphuric acid.

Chromic anhydride forms scarlet needles and melts without decomposition at 196°. At 250° it loses oxygen and gives **chromic chromate,** Cr_2O_3,CrO_3, and at higher temperatures it is converted into chromic oxide, Cr_2O_3. It dissolves readily in water, its solubility being almost independent of the temperature ; thus, a saturated solution in water contains 57 per cent. of CrO_3 at — 105° (the eutectic temperature) and 71 per cent. of CrO_3 at 127° ; by cooling a warm saturated solution of the trioxide in water, **chromic acid,** H_2CrO_4, can be crystallised out in rose-red crystals which decompose when warmed. The trioxide is almost insoluble in sulphuric acid of density 1·77 and in ordinary concentrated nitric acid ; but it is soluble in acetic acid and in ether.

Chromic anhydride is a powerful oxidising agent and is used largely in organic chemistry ; it inflames anhydrous alcohol, but when suitably diluted oxidises it to aldehyde,

$$C_2H_6O + O = C_2H_4O + H_2O.$$

Potassium dichromate, in presence of sulphuric acid, is also used in volumetric analysis to oxidise ferrous iron,

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = 2KCr(SO_4)_2 + 3Fe_2(SO_4)_3 + 7H_2O.$$

The metallic chromates are described below.

Halogen Derivatives and Amides.

Chromyl chloride, CrO_2Cl_2, prepared by distilling potassium dichromate with salt and sulphuric acid, is analogous to sulphuryl chloride, SO_2Cl_2. It is a heavy blood-red liquid, resembling bromine, its density being just under 2. It boils at 116°, and gives a vapour density corresponding with the formula CrO_2Cl_2. It sinks in water, but is soon decomposed into chromic anhydride and hydrochloric acid,

$$CrO_2Cl_2 + H_2O = CrO_3 + 2HCl.$$

Chromyl fluoride, CrO_2F_2, has been prepared, but bromine and iodine do not form compounds of this type ; the vaporisation of chromium under the conditions described above can therefore be used to separate chlorine from bromine and iodine.

Potassium chlorochromate, $Cl.CrO_2.OK$, a compound intermediate between potassium chromate, $CrO_2(OK)_2$, and chromyl chromide, CrO_2Cl_2, can be prepared by the action of hydrochloric acid on potassium dichromate or of potassium chloride on chromyl chloride.

$$K_2Cr_2O_7 + 2HCl = 2KCrO_3Cl + H_2O$$

$$\text{or } CrO_2Cl_2 + KCl + H_2O = KCrO_3Cl + 2HCl.$$

It separates in red prisms and is decomposed partially by water, but can be recrystallised in presence of hydrochloric acid. Ammonia in presence of ether converts it into **potassium amidochromate,** $NH_2.CrO_2.OK$, from which **chromyl diamide,** $CrO_2(NH_2)_2$, can be prepared by the action of chlorine and ammonia.

Chromates and Dichromates.

The first stage in working up chrome iron ore with the view of preparing pure compounds of chromium is to convert the chromite into a chromate by atmospheric oxidation in presence of an alkali or of lime, the chromate being usually crystallised out in the form of potassium dichromate. Compounds of tervalent chromium are then prepared by reduction of the sexavalent compounds.

Potassium dichromate, $K_2Cr_2O_7$, is prepared by heating finely-powdered chromite in a reverberatory furnace (p. 690), with potassium

carbonate or sulphate or with potash-felspar in order to convert the ferrous chromite into potassium chromate,

$$4FeCr_2O_4 + 8K_2CO_3 + 7O_2 = 2Fe_2O_3 + 8K_2CrO_4 + 8CO_2;$$

the "melt" is broken up and extracted with water by a counter-current process which yields a solution saturated with the normal potassium chromate; on adding sulphuric acid to convert the chromate into the dichromate,

$$2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O,$$

the latter salt (which is much less soluble) crystallises out and is purified by recrystallisation from water. Alternatively, potassium dichromate can be prepared by heating a mixture of chromite and chalk, adding sulphuric acid to convert the calcium chromate to dichromate, and precipitating the remainder of the calcium by adding potassium carbonate and then crystallising out the potassium dichromate.

Potassium dichromate is a red salt, crystallising in the asymmetric system. It melts without decomposition at 396°, but breaks down at a red heat, losing oxygen and giving potassium chromate and chromic oxide,

$$4K_2Cr_2O_7 = 4K_2CrO_4 + 2Cr_2O_3 + 3O_2.$$

A saturated solution in water contains 4·4 per cent. of the dichromate at 0°, 50·5 per cent. at 100°, and 72·5 per cent. under pressure at 180°; the chromate is less soluble than the dichromate in hot water, but much more so in cold water, the saturated solution containing 44 per cent. of the chromate at 100° and 36 per cent. at 0°.

Potassium dichromate is an oxidising agent, *e.g.*, it will oxidise sulphur to potassium sulphate either in presence of boiling water or by fusion,

$$K_2Cr_2O_7 + S = K_2SO_4 + Cr_2O_3.$$

It is, however, used more frequently in conjunction with sulphuric acid, as in the dichromate battery (p. 196) and in the oxidation of ferrous sulphate and of organic compounds (see under Chromic Acid, p. 742). It forms insoluble products with gelatine and with gum when exposed to light; these are used in photography as the basis of the CARBON PROCESS and the GUM DICHROMATE PROCESS of printing, the gelatine or gum being mixed with a pigment, exposed under a negative, and developed by washing away the unchanged material with hot water. Potassium dichromate is also the material from which chromium pigments and chromium compounds in general are prepared.

Potassium chromate, K_2CrO_4, is a yellow salt, isomorphous with potassium sulphate, K_2SO_4. It can be prepared from chromite, or by the action of potassium hydroxide on the dichromate, but even carbon dioxide reconverts it into the dichromate,

$$2K_2CrO_4 + CO_2 = K_2Cr_2O_7 + K_2CO_3.$$

The dust is toxic, and special precautions are needed to protect workers who are handling this salt.

Sodium chromate, $Na_2CrO_4,10H_2O$, is isomorphous with the sulphate, $Na_2SO_4,10H_2O$; the **decahydrate** changes into a **hexahydrate** at 19·525° (compare the transition temperature for sodium sulphate at 32·383°, p. 578), and into a **tetrahydrate** at 25·90°, whilst above 68° the anhydrous salt separates from solution. A saturated solution contains 24 per cent. of Na_2CrO_4 at 0° and 56 per cent. at 100°, as compared with 36 and 44 per cent. of K_2CrO_4; the decahydrated sodium salt is, however, much more soluble than the anhydrous potassium salt, even at 0°. **Sodium dichromate,** $Na_2Cr_2O_7$, crystallises from water as a **dihydrate** up to 83°, but is anhydrous above this temperature; unlike the potassium salt, it is more soluble than the corresponding chromate, since a saturated solution contains 62 per cent. of $Na_2Cr_2O_7$ at 0° and about 81 per cent. in the range from 83° to 100°, where the solubility of the anhydrous salt is almost constant. On account of its lower cost, sodium dichromate is often used instead of the potassium salt, and in many cases its greater solubility is also a marked advantage.

Ammonium dichromate, $(NH_4)_2Cr_2O_7$, prepared from ammonia and chromic acid, decomposes when heated and gives a bulky residue of chromic oxide.

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4H_2O.$$

Calcium chromate, $CaCrO_4,4H_2O$, is an intermediate product in some processes for making potassium dichromate; it is soluble in water, but becomes almost insoluble when dehydrated at 200° (compare $CaSO_4$, p. 637, and $MgSO_4.H_2O$, p. 622).

Barium chromate, $BaCrO_4$, is insoluble in water, like barium sulphate, and is used as a pigment under the name of LEMON-YELLOW.

Lead chromate, $PbCrO_4$, like lead sulphate, is insoluble in water, but is dissolved by *cold* lime water or alkali hydroxides. It is found as CROCOITE, a red mineral which gives an orange-yellow streak. It is manufactured by precipitation from lead acetate by the addition of a chromate and is used as a pigment under the name of CHROME YELLOW; when precipitated with lead sulphate as a diluent, it is known as COLOGNE YELLOW, whilst mixtures with Prussian blue are known as BRUNSWICK GREEN, or sometimes as "chrome green," a name that should be reserved for the sesquioxide. Boiling with a caustic alkali or with lime converts the yellow chromate into a **basic chromate,** $PbO,PbCrO_4$; this has a red colour and is used as a pigment under the name of CHROME RED, *e.g.*, for painting letter-boxes; intermediate grades are known as CHROME ORANGE.

Zinc chromate, $ZnCrO_4$, is a beautiful yellow pigment which does not blacken when exposed to hydrogen sulphide; it is used mainly as a mixture with Prussian blue under the name of ZINC GREEN.

Perchromic Acid.

When an aqueous solution of chromium trioxide is mixed with hydrogen peroxide a dark solution is produced from which a blue product can be extracted with ether. This blue colour, which forms a very sensitive test both for chromium and for hydrogen peroxide, is attributed to a perchromic acid, the formula of which is not quite certain. By adding organic bases such as pyridine, C_5H_5N, to the cold ethereal solution, salts derived from the **perchromic acid,** $HCrO_5$, have been prepared, *e.g.*, $(C_5H_6N)CrO_5$. By the addition of ammonium and potassium salts, PERCHROMATES of the formulæ NH_4CrO_5,H_2O_2 and $KCrO_5,H_2O_2$ have been separated; these are commonly regarded as containing "hydrogen peroxide of crystallisation," but they may be derivatives of a perchromic acid of the formula H_3CrO_7. A red **ammonium perchromate** of the formula $(NH_4)_3CrO_8$, has been prepared by the action of hydrogen peroxide on the chromate in alkaline solution; when acidified, this loses oxygen and gives the blue **ammonium salt,** $(NH_4)H_2CrO_7$, already described, from which in turn the **pyridine salt,** $(C_5H_6N)CrO_5$, can be prepared by loss of another atom of oxygen; finally, all these compounds with an excess of ammonia give **chromium tetroxide triammine,** $CrO_4,3NH_3$.

Detection and Estimation of Chromium.

Chromium can be detected and estimated either as a tervalent chromic salt or as a chromate; the conversion of the yellow colour of a chromate into the green colour of a chromic salt on reduction, and the converse change of colour on oxidation, are conclusive evidence of the presence of chromium. Thus, chromium compounds give an emerald-green borax bead, but on fusion with sodium carbonate and sodium nitrate give a yellow mass of sodium chromate.

Chromic salts give a green precipitate of **chromic hydroxide,** $Cr(OH)_3$, with ammonia even in the presence of ammonium chloride. This differs from ferric hydroxide in dissolving in an excess of cold potassium hydroxide, and from aluminium hydroxide in that it is precipitated again by boiling the solution. Chromates are recognised by their yellow colour and by giving with silver nitrate a red precipitate of **silver chromate,** Ag_2CrO_4, which dissolves readily both in ammonia and in dilute nitric acid. Barium chloride gives a yellow precipitate of **barium chromate,** $BaCrO_4$, and lead acetate or nitrate gives a yellow precipitate of **lead chromate,** $PbCrO_4$, or chrome yellow, which is turned into chrome red by boiling with alkalies. Chromates can also be detected by giving **chromyl chloride,** CrO_2Cl_2, when distilled with salt and sulphuric acid, and by giving a blue colour of **perchromic acid,** $HCrO_5$, to ether on oxidation in acid solution with hydrogen peroxide.

Chromium is estimated gravimetrically as the **sesquioxide,** Cr_2O_3, by precipitating with ammonia and igniting; chromates may be

estimated in this way after reduction with sulphur dioxide or may be precipitated and weighed as **lead chromate.**

Chromates are estimated volumetrically by titration against a ferrous salt, and this method can be applied to the estimation of chromium in minerals, after fusing them with an alkali and an oxidising agent.

The atomic weight of chromium is based mainly on determinations of the proportion of silver in silver chromate, Ag_2CrO_4, and in silver dichromate, $Ag_2Cr_2O_7$, giving the ratios $Ag_2CrO_4 : 2Ag$ and $Ag_2Cr_2O_7 : 2Ag$

42. MOLYBDENUM. Mo = 96·0.

Molybdenum.

(*a*) *Occurrence.*—Molybdenum occurs as **molybdenum disulphide,** MoS_2, in the form of MOLYBDENITE, a soft grey mineral with a brilliant metallic lustre (compare stibnite, Fig. 251, p. 707), which resembles graphite so closely that it has sometimes been mistaken for and used instead of graphite. It also appears as the acid constituent of **calcium molybdate,** $CaMoO_4$, and **lead molybdate,** $PbMoO_4$, two almost colourless crystalline minerals which are isomorphous with the corresponding tungstates, $CaWO_4$, $PbWO_4$.

(*b*) *Separation.*—The element is usually separated in the form of **molybdenum trioxide,** MoO_3; this occurs in a hydrated form as MOLYBDIC OCHRE, and can be prepared as a sublimate by heating the native sulphide in a current of air. More usually, the sulphide ore is roasted, and the trioxide extracted with dilute ammonia, and separated as **ammonium molybdate,** from which it can be recovered, after purification, by evaporating the ammonium salt with nitric acid and igniting the residue. Ammonium molybdate can also be prepared from the mineral molybdates and the trioxide separated from it by ignition.

(*c*) *Metallic Molybdenum.*—The metal is prepared in a solid form as a powder by reducing the oxide with carbon in an electric furnace. It is strong and ductile, and can be welded and drawn into filaments. It has been used recently as a substitute for tungsten in self-hardening tool steels (p. 777). It is insoluble in dilute hydrochloric and sulphuric acids, but dissolves in oxidising acids, such as dilute nitric acid and concentrated sulphuric acid, and burns to the trioxide at a red heat.

(*d*) *Compounds of Molybdenum.*—**Molybdenum trioxide,** MoO_3, prepared as described above, is a white powder which is slightly soluble in water and imparts to it a metallic taste and an acid reaction; it is, however, readily soluble in ammonia. **Molybdic acid,** H_2MoO_4, crystallises out slowly from a solution of the ammonium salt in nitric acid, whilst from dilute nitric acid a **monohydrate,** H_2MoO_4,H_2O, separates. The acid forms a series of simple MOLYBDATES, *e.g.*,

Na_2MoO_4	K_2MoO_4	$(NH_4)_2MoO_4$,
$CaMoO_4$	$BaMoO_4$	$PbMoO_4$,

but complex salts containing a large excess of molybdic acid, *e.g.*, up to 10Mo, are also commonly produced. **Ammonium molybdate** (usually $6NH_3,7MoO_3,7H_2O$, *i.e.*, $(NH_4)HMoO_4$ with a slight deficiency of ammonia) is used in analysis for detecting and separating phosphoric acid. **Ammonium phosphomolybdate,** $(NH_4)_3PO_4,10MoO_3$, which is obtained as a yellow precipitate by the action of phosphoric acid on a solution of ammonium molybdate in nitric acid, dissolves readily in aqueous ammonia, or when an excess of phosphoric acid is present. Other compounds of molybdenum include the *halogen derivatives,*

MoF_6, $MoCl_5$, $MoCl_4$, $MoCl_3$, $MoCl_2$, $MoOF_4$, MoO_2F_2, and $2KF,MoO_2F_2,H_2O$ or $K_2MoO_2F_4,H_2O$ (compare $K_2WO_2F_4$),

and *salts* in which the oxides Mo_2O_3 and MoO_2 act as bases.

74. TUNGSTEN. W = 184·0.

Tungsten.

(*a*) *Occurrence.*—Tungsten (or wolfram, as the element is also called) is found as **tungsten trioxide,** WO_3, in the form of WOLFRAM OCHRE. **Calcium tungstate,** $CaWO_4$, **lead tungstate,** $PbWO_4$, **manganese tungstate,** $MnWO_4$, and **copper tungstate,** $CuWO_4$, are also found as minerals. The most important ore of tungsten is, however, WOLFRAMITE, an isomorphous **ferrous-manganese tungstate,** $[Fe,Mn]WO_4$, which is found in Cornwall and elsewhere, usually associated with cassiterite or tin-stone, SnO_2; on account of their similar high densities these two minerals cannot be separated by washing, but are separated by taking advantage of the magnetic properties of wolframite.

Cassiterite and zircon are isomorphous with one another and crystallise in the tetragonal system, to which the molybdates and tungstates also belong, although their axial ratios are different; these compounds may therefore be tabulated in two groups, one containing two quadrivalent metallic atoms, and the other one bivalent and one sexavalent atom.

Cassiterite, SnO_2 or $SnSnO_4$.	*Scheelite,* $CaWO_4$.
Zircon, $ZrSiO_4$.	*Wolframite,* $FeWO_4$.
Also TiO_2 or $TiTiO_4$ and $ThSiO_4$.	Also $CaMoO_4$ and $PbMoO_4$.

(*b*) *Separation.*—Tungsten is usually extracted from its ores in the form of **sodium tungstate,** $Na_2WO_4,2H_2O$; this is prepared by roasting the ore to remove sulphur, arsenic, and phosphorus, and heating it with "soda ash" (sodium carbonate) under such conditions that the tin and silica, as well as iron, manganese, and copper, remain undissolved when the tungstate is dissolved out in water, filtered from insoluble impurities, and purified by recrystallisation.

(*c*) *Metallic Tungsten.*—FERRO-TUNGSTEN, containing up to 80 per

cent. of tungsten alloyed with iron, can be prepared by direct reduction from wolframite which is low in manganese. In order to separate the pure metal from its ores, tungstic acid is precipitated from crude sodium tungstate, dried, mixed with carbon, and reduced to a solid metallic powder, without fusion, by heating strongly in a furnace. The metal (density 19·1) is nearly as dense as gold and melts at a higher temperature than any other metal, namely, about 3060°; it can therefore be melted and vaporised only in the electric furnace. The metal can, however, be welded by hammering, and drawn out into filaments, which are now employed universally in electric lamps; since tungsten combines both with oxygen and with nitrogen, tungsten-filament lamps are either exhausted, or filled with argon, as in the "half-watt" lamp. Metallic tungsten is also the most important constituent of self-hardening steel tools (p. 777), which may contain from 12 to 18 per cent. of this element, whilst the steel used for making valves for internal combustion engines may contain about 3 per cent. of tungsten.

Ductile tungsten is prepared by pressing the powder into rods, which are then made compact by heat, the particles being sintered together by the passage of an electric current. Even in this condition the metal is quite brittle, and ductility is only obtained by "swaging" under a series of centrifugal hammers at a very high temperature after heating in hydrogen. The swaging is followed by drawing, the metal becoming progressively more ductile until it can be bent or drawn cold. Finally, a filament is obtained which is only 0·0011 inch in diameter, but has a tensile strength of nearly 270 tons per square inch, exceeding that of all other metals and alloys that have been examined. Tungsten differs from other metals in being more ductile when cold after severe working and deformation than in the annealed condition. The possibility of drawing tungsten cold depends on the size of the grains of the original sintered ingot, which must be below a certain limiting average size; on long exposure to high temperatures, as when used in lamp filaments, the grains tend to grow in size and thus render the filament brittle; this tendency is checked by mixing a small quantity of thorium dioxide with the tungsten-powder in making the original ingot, since the infusible and non-volatile particles of this oxide present an obstacle to the growth of the grains.

(*d*) *Compounds of Tungsten.*—**Tungstic acid,** like molybdic acid, may be separated in two forms as H_2WO_4 and H_2WO_4,H_2O. It forms a series of normal TUNGSTATES, several of which are found as minerals; but like vanadium and molybdenum it forms complex tungstates containing up to 12W. Other compounds of tungsten include the

chlorides, WCl_2, WCl_4, WCl_5, WCl_6;
fluorides and *oxyfluorides*, WF_6, WOF_4, and $K_2WO_2F_4,H_2O$;
nitride, phosphides, and *sulphides*, W_2N_3; W_2P, WP, WP_2 and W_3P_4; WS_2 and WS_3;
boride, carbides, and *silicide*, WB_2; WC, W_2C; W_2Si_3.

92. URANIUM. U = 238·2.

Uranium.

(*a*) *Occurrence.*—Uranium is found as **potassium uranyl vanadate,** $K(UO_2)VO_4,1\frac{1}{2}H_2O$, in CARNOTITE, and as **calcium uranyl phosphate,** $Ca(UO_2)_2(PO_4)_2,8H_2O$, in AUTUNITE. The principal source of the element is, however, URANINITE OF PITCHBLENDE, a mineral of complex composition which contains about 80 per cent. of the **oxide,** U_3O_8, together with oxide of lead, PbO, ferric oxide, Fe_2O_3, thorium dioxide, ThO_2, and the oxides of the rare earths. Pitchblende is also the source from which radium is derived (p. 904), and it was in a mineral of this character that terrestrial helium was first discovered (p. 365). The radioactivity of uranium and its conversion by atomic disintegration into radium, lead, and helium are discussed in Chapter XLV.

(*b*) *Separation.*—The simplest method of separating uranium from pitchblende is to digest the powdered mineral with nitric acid and to evaporate the solution to dryness; **uranyl nitrate,** $UO_2(NO_3)_2$, is then extracted from the residue and purified first by recrystallising the hexahydrate from water, and then by dissolving the anhydrous salt in ether. The uranium can also be separated from pitchblende in the form of **ammonium diuranate,** $(NH_4)_2U_2O_7$.

In the commercial method of separation, the ore is first roasted and then heated in a reverberatory furnace with sodium carbonate and a little sodium nitrate, in order to convert the uranium into a uranate, just as chromium is converted into a chromate in order to separate it from its ores. The fused mass is washed with water and the uranium is then extracted with dilute sulphuric acid, as **uranyl sulphate,** $(UO_2)SO_4$, leaving an insoluble residue from which radium can be separated. On adding an excess of sodium carbonate, iron, aluminium, etc., are precipitated, whilst the uranium remains in solution, and is finally thrown down as **sodium diuranate,** $Na_2U_2O_7,6H_2O$, by the addition of sodium hydroxide.

(*c*) *Metallic Uranium.*—The metal is prepared in much the same way as molybdenum and tungsten, by heating the oxide, U_3O_8, with sugar charcoal in an electric furnace. It is a white metal of high density (18·7) and melting-point (about 1800°), but can be melted and distilled in the electric furnace. The powdered metal oxidises in air, decomposes water, burns in oxygen at 160° and in chlorine at 150°, and unites directly with sulphur and nitrogen.

(*d*) *Compounds of Uranium.*—Uranium forms two principal series of compounds, namely,

(i) Quadrivalent URANOUS SALTS derived from the basic oxide, UO_2, *e.g.*, UCl_4, $U(SO_4)_2$, etc.

(ii) Hexavalent compounds derived from the amphoteric oxide, UO_3, including on the one hand URANYL SALTS such as UO_2Cl_2, $UO_2(NO_3)_2$, $(UO_2)SO_4$, etc., in which the bivalent URANYL RADICAL, UO_2'', acts as a metal (compare VO'''), and

on the other hand URANATES such as Na_2UO_4, and DIURANATES such as $Na_2U_2O_7$, corresponding with the chromates and dichromates.

The most stable of the oxides, to which the formula U_3O_8 is given, is probably a compound, $UO_2,2UO_3$, of these two oxides; it is formed as a dark green, almost black, powder when the other oxides are ignited in air or when ammonium uranate is ignited.

Uranium dioxide, UO_2, is prepared by reducing the oxide, U_3O_8, in a current of hydrogen; it can be obtained in black crystals and was at first mistaken for the metal (compare vanadium and its homologues). When ignited in a current of hydrogen chloride it gives **uranous chloride,** UCl_4, a deliquescent compound which sublimes at a red heat in dark-green octahedra; but when heated in a current of chlorine addition takes place instead of substitution, and **uranyl chloride,** UO_2Cl_2, is formed as a red vapour which condenses in fusible yellow crystals; the monohydrate, UO_2Cl_2,H_2O, can be prepared by dissolving the dioxide in aqua regia. When heated in air the dioxide burns again to the mixed oxide, U_3O_8.

Uranium trioxide, UO_3, can be prepared as a yellow or red powder by heating uranyl nitrate, $UO_2(NO_3)_2$, at 250°, just as litharge can be prepared by heating lead nitrate. It acts as an acid towards strong bases, with which it forms a series of URANATES, and as a base towards strong acids, with which it forms URANYL SALTS, in which only one of its oxygen atoms is replaced by acid radicals. The most important of the uranates is **sodium diuranate,** $Na_2U_2O_7$, compare sodium dichromate, $Na_2Cr_2O_7$; it is known as URANIUM YELLOW, and is used in painting glass and porcelain and in making the yellow fluorescent URANIUM GLASS. It is prepared by roasting pitchblende with lime and converting the calcium uranate first into uranyl sulphate and then into sodium uranate. **Ammonium diuranate,** $(NH_4)_2U_2O_7$, is formed as a yellow precipitate by adding ammonia to a solution of a uranyl salt; it dissolves again in mineral acids as a uranyl salt, and is also soluble in ammonium carbonate, perhaps as **ammonium uranate,** $(NH_4)_2UO_4$.

When the oxide, U_3O_8, is dissolved in sulphuric acid it gives **uranous sulphate,** $U(SO_4)_2,9H_2O$, a compound which is isomorphous with thoric sulphate, $Th(SO_4)_2,9H_2O$, and forms double salts such as $U(SO_4)_2,2K_2SO_4,2H_2O$, or $K_4U(SO_4)_4,2H_2O$, compare $Th(SO_4)_2,2K_2SO_4,2H_2O$, in which the two metals are present in equivalent quantities as in $K_2Mg(SO_4)_2,6H_2O$ (p. 622) and $K_3Ce(SO_4)_3$ (p. 670).

Uranyl sulphate, $UO_2SO_4,3H_2O$, is also formed in this action, and remains in the mother-liquor when uranous sulphate is precipitated by addition of alcohol. It can be prepared more readily by heating uranyl nitrate with sulphuric acid and forms double salts, like magnesium sulphate, ferrous sulphate, etc. (p. 725).

Uranyl nitrate, $UO_2(NO_3)_2,6H_2O$, is prepared by dissolving any of the oxides of uranium in nitric acid; it crystallises in yellow fluorescent prisms and is one of the principal salts of the metal. It can be prepared by igniting ammonium uranate and dissolving the oxide in nitric acid, or more directly by the action of nitric acid on pitchblende as described above.

Uranyl acetate, $UO_2(C_2H_3O_2)_2,2H_2O$, gives with phosphoric acid in presence of an ammonium salt **uranyl ammonium phosphate,** $UO_2(NH_4)PO_4$; compare $MgNH_4PO_4$. This compound is formed when uranous acetate and a soluble

phosphate are titrated against one another, in presence of an ammonium salt, potassium ferrocyanide being used as an external indicator to detect an excess of the uranyl acetate, with which it gives a brown coloration.

The binary compounds of uranium include three chlorides of the formulæ UCl_3, UCl_4, and UCl_5, a monosulphide, US, and a sesquisulphide, U_2S_3, a nitride, U_3N_4, and a carbide, U_2C_3.

(*e*) *Detection and Estimation of Uranium.*

In qualitative analysis uranium is precipitated with aluminium, by the action of ammonia and ammonium chloride, as **ammonium diuranate**, $(NH_4)_2U_2O_7$. Ammonium sulphide gives a red-brown precipitate of **uranyl sulphide**, $(UO_2)S$. When an excess of sodium or ammonium carbonate is present, uranium remains in solution on adding ammonia or ammonium sulphide, but is precipitated quantitatively (with magnesium) as **ammonium uranyl phosphate**, $NH_4(UO_2)PO_4$, on the addition of a phosphate. It is also precipitated quantitatively as **potassium uranyl ferrocyanide**, $K_2(UO_2)_3(FeC_6N_6)_2$, by potassium ferrocyanide, which is therefore used as an indicator when uranyl acetate is titrated against phosphoric acid or a phosphate.

Uranium is estimated gravimetrically by precipitating as $(NH_4)_2U_2O_7$ and igniting to U_3O_8. It can also be deposited (like manganese and lead) as a peroxide at the anode in electro-analysis, and converted to U_3O_8 by ignition. The volumetric estimation (in the absence of iron) depends on reducing uranyl compounds to uranous salts by zinc, magnesium, or aluminium in presence of sulphuric acid, *e.g.*,

$$(UO_2)SO_4 + Zn + 2H_2SO_4 = ZnSO_4 + U(SO_4)_2 + 2H_2O,$$

and oxidising back with potassium permanganate,

$$U(SO_4)_2 + O + H_2O = (UO_2)SO_4 + H_2SO_4;$$

compare $$2FeSO_4 + O + H_2SO_4 = Fe_2(SO_4)_3 + H_2O.$$

Uranyl salts may also be titrated against a phosphate (see above).

CHAPTER XL

MANGANESE

Atomic number.	*Element.*	*Symbol.*		*Atomic weight.*
25	Manganese	Mn	=	54·93
43	*eka*-Manganese*	*Em*	=	*100* ?
75	*tri*-Manganese*	*Tm*	=	*188* ?

Occurrence of Manganese.

After the common bases, Al_2O_3, CaO and MgO, Na_2O and K_2O, FeO and Fe_2O_3, the most abundant metallic oxides in igneous rocks are baryta, BaO, and manganous oxide, MnO, although these are present only to the extent of about 0·1 per cent. as compared with from 3 to 15 per cent. of the oxides of the six preceding metals. Manganese is distributed somewhat widely in ferromagnesian minerals as an isomorphous impurity in ferrous silicates. Like iron, it is removed in the form of a bicarbonate, $Mn(CO_3H)_2$, when these rocks are destroyed by weathering, and is precipitated, as the result of oxidation, as an amorphous oxide containing variable proportions of water; but whereas the iron is oxidised to the sesquioxide and thrown down as limonite, Fe_2O_3 aq., the manganese is precipitated as **manganese dioxide,** MnO_2, or PYROLUSITE. Nodules rich in manganese are a characteristic deposit in deep oceanic waters. MANGANITE, a **hydrated sesquioxide,** Mn_2O_3,H_2O, or $HMnO_2$, is similar in crystalline form and probably isomorphous with göthite, the only crystalline hydrated oxide of iron, Fe_2O_3,H_2O or $HFeO_2$, compare diaspore, $HAlO_2$, but is liable to change into pyrolusite. The **oxides,** Mn_3O_4 and MnO, and the **sulphides,** MnS and MnS_2, are also found as ores, but are much less common.

Preparation of Manganese.

Metallic manganese, like metallic chromium, can not be prepared readily by reducing the oxide. Reduction can, however, be effected

* These names were given by Mendeléeff to the unknown homologues of manganese, which are still included amongst the missing elements (p. 539).

by igniting an intimate mixture of manganese dioxide and lamp black with a suitable slag in crucibles at a white heat,

$$MnO_2 + 2C = Mn + 2CO,$$

or by reduction with carbon in the electric furnace. As in the case of chromium, the metal prepared by the latter process contains a large proportion of carbon, which may be removed by remelting the crude metal with the oxide. Pure manganese is now prepared by reducing the oxide with aluminium (Goldschmidt process), but very large quantities of FERRO-MANGANESE, *i.e.* an alloy of iron and manganese, are prepared by reducing mixed ores of iron and manganese in the blast furnace.

Properties of Manganese.

(*a*) *Physical Properties.*—Manganese melts at a much lower temperature than the other metals of the iron group, as may be seen in the following table :—

TABLE 87.—MELTING-POINTS OF STEEL-FORMING METALS.

	Melting-point.	*Metal.*	*Melting-point.*
Vanadium	1720°	Cobalt	1480°
Chromium	1615°	Nickel	1452°
Iron	1530°	Manganese	1230°

The difficulty of smelting manganese arises from the fact that, instead of giving an eutectic alloy with carbon, it forms a series of solid solutions with the **carbide,** Mn_3C; this melts at a temperature within a few degrees of the melting-point of the metal, namely at 1217°, and instead of lowering the melting-point of pure manganese, actually raises it slightly (Fig. 255).

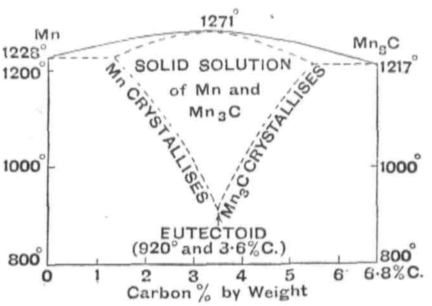


FIG. 255.—FREEZING-POINT DIAGRAM FOR MANGANESE AND MANGANESE CARBIDE.

(*b*) *Alloys.* — Pure manganese is a comparatively soft metal, but in presence of carbon it becomes very hard; and one of the principal features of the manganese steels (Fig. 202, p. 524) is their extreme toughness and resistance to wear. Manganese forms a complete series of solid solutions with γ-iron, as well as with copper and nickel, but the two latter series are remarkable in showing a minimum melting-point (Fig. 256), whilst solid solutions with the carbide, Mn_3C, show a maximum. Manganese forms two very stable **phosphides,** Mn_5P_2 and MnP,

and two stable **silicides,** Mn_2Si and MnSi, all melting at temperatures not far removed from the melting-point of the metal; the **sulphide,**

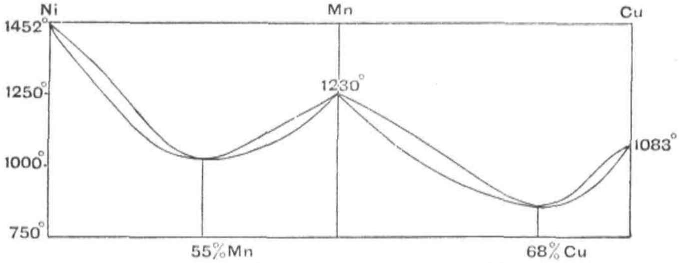


FIG. 256.—FREEZING-POINT DIAGRAM FOR ALLOYS OF MANGANESE WITH NICKEL AND COPPER.

MnS, is also a compound of high melting-point, which is only sparingly soluble in metallic iron, a property which is used largely in desulphurising iron by the addition of manganese (p. 766).

Chemical Properties of Manganese.

Manganese oxidises readily, especially when it contains carbon, since the carbide decomposes in moist air, as shown in the equation

$$Mn_3C + 6H_2O = 3Mn(OH)_2 + CH_4 + H_2.$$

It is remarkable for the long series of oxides which it forms, the lowest being strongly basic, whilst the highest are strongly acidic.

TABLE 88.—OXIDES OF MANGANESE.

Compound.	*Formulæ.*	*Character of Oxide.*
Manganous oxide	MnO	Strong base
Manganic oxide	Mn_2O_3	Weak base
Manganese dioxide	MnO_2	Amphoteric oxide forming salts both with acids and with bases
Manganese trioxide	MnO_3	Acid
Dimanganese heptoxide	Mn_2O_7	Acid.

In presence of acids, the bivalent manganous compounds derived from the *monoxide* are the most stable; under neutral conditions manganese *dioxide* is generally formed; and fusion with alkalies results in oxidation to manganates derived from the *trioxide.*

Manganese and Oxygen.

Manganous oxide, MnO, is formed by igniting the higher oxides or the carbonate in a current of hydrogen, just as ferrous oxide can be formed from ferric oxide by cautious reduction in hydrogen.

Manganic oxide, Mn_2O_3, is found in brownish-black octahedra,

and also in a crystalline hydrated form as MANGANITE, Mn_2O_3,H_2O or $HMnO_2$, compare $HAlO_2$ and $HFeO_2$.

Manganese dioxide, MnO_2, occurs as PYROLUSITE, occasionally in crystals, but more frequently in a massive form; an impure earthy variety is known as WAD. When heated, it loses one-third of its oxygen and gives **trimanganese tetroxide,** Mn_3O_4; this is a reddish-brown compound which occurs as a mineral under the name of HAUSMANNITE; it may be regarded as an orthomanganite, Mn_2MnO_4 (compare Mg_2SiO_4), containing manganous oxide as the base and manganese dioxide as the acid. In the same way, the sesquioxide, Mn_2O_3, may be regarded as a metamanganite, $MnMnO_3$ (compare $MgSiO_3$), analogous to **ferrous manganite,** $FeMnO_3$, which is found as a mineral, and **calcium manganite,** $CaMnO_3$, which is formed in the "Weldon recovery process" (p. 269).

Manganese dioxide does not dissolve readily in dilute acids unless reducing agents are present; it therefore dissolves more easily in sulphurous acid than in sulphuric acid,

$$MnO_2 + SO_2 = \underset{\text{Manganous sulphate}}{MnSO_4}; \quad MnO_2 + 2SO_2 = \underset{\text{Manganous dithionate}}{MnS_2O_6}.$$

When baked with sulphuric acid, however, it loses half its oxygen and gives manganous sulphate,

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + O_2 + 2H_2O.$$

Hydrochloric acid dissolves it at low temperatures, giving a green solution from which the dioxide can be reprecipitated by water; but, on warming, chlorine is set free and manganous chloride, $MnCl_2$, is formed, perhaps as shown in the following equations, where the tetrachloride, $MnCl_4$ (p. 757), is shown as an intermediate product,

$$MnO_2 + 4HCl \rightleftharpoons MnCl_4 + 2H_2O,$$
$$MnCl_4 = MnCl_2 + Cl_2.$$

Manganese dioxide also dissolves readily in presence of ammonium salts, which are oxidised by it; thus it dissolves in ammonium nitrate and nitric acid, liberating nitrogen as shown in the equation,

$$3MnO_2 + 2NH_4NO_3 + 4HNO_3 = 3Mn(NO_3)_2 + N_2 + 6H_2O.$$

Manganese dioxide is the principal source of manganese for use in the manufacture of steel and in the preparation of manganese compounds of all kinds. It is used as an oxidising agent in the preparation of chlorine (p. 269) and as a depolariser to oxidise hydrogen in the Leclanché battery (p. 196), for which purpose its marked electrical conductivity is important; its oxidising action in the battery may perhaps be represented by the equation

$$Zn + 2NH_4Cl + MnO_2 = ZnCl_2,2NH_3 + Mn(OH)_2.$$

In the paint and varnish industry manganese dioxide is added to "drying oils," apparently as a catalyst to promote the absorption of

oxygen by these oils and their conversion to resinous oxidation-products. Manganese dioxide is used to neutralise the green tint in glass containing ferrous silicates; these are oxidised to yellow ferric compounds and then masked by the blue colour of the manganese silicates which are formed. The higher acid-forming oxides of manganese are described below.

Manganese and Sulphur.

Manganous sulphide, MnS (see also p. 754), is formed as a flesh-coloured precipitate by the action of ammonium sulphide on a solution of a manganous salt. It is also found as a rare mineral in steel-grey cubic crystals, isomorphous with blende, ZnS, and troilite, FeS.

Manganese disulphide, MnS_2, is also found as a rare mineral in cubic crystals with a metallic lustre, of the same type as iron pyrites, FeS_2.

Manganous Salts.

Manganous chloride, $MnCl_2$, is formed as a by-product in the preparation of chlorine from manganese dioxide and hydrochloric acid.

In order to separate the chloride, the solution is concentrated to remove hydrochloric acid, part of the manganese is precipitated as manganous carbonate by adding sodium carbonate, and this precipitate is used to eliminate iron as ferric hydroxide from the remainder of the solution,

$$3MnCO_3 + 2FeCl_3 + 3H_2O = 3MnCl_2 + 2Fe(OH)_3 + 3CO_2.$$

Copper can be precipitated by sulphuretted hydrogen, and cobalt and nickel by contact with manganous sulphide, MnS. The manganese is then precipitated by ammonium sulphide, washed, and redissolved in hydrochloric acid.

Manganese chloride is a soluble deliquescent salt. It separates from water in pink crystals with $4H_2O$. These are used in dyeing, manganese dioxide being formed by precipitating manganous hydroxide on the fibres and oxidising it to the dioxide by atmospheric oxygen.

Manganous sulphate, $MnSO_4$, is prepared by baking manganese dioxide with sulphuric acid at a temperature high enough to decompose ferrous sulphate. It separates from water in pink crystals with $7H_2O$ up to 9°, $5H_2O$ from 9° to 27°, and $1H_2O$ above 27°; the solubility of the monohydrate diminishes as the temperature rises. It also forms the usual series of **double sulphates** of the type $K_2SO_4,MnSO_4,6H_2O$.

Manganous nitrate, $Mn(NO_3)_2,6H_2O$, is a soluble deliquescent salt.

Manganous carbonate, $MnCO_3$, in the form of RHODOCROSITE, is isomorphous with calcite; but it may also exist as an isodimorphous impurity in carbonates of the aragonite type (p. 630).

Manganic Salts.

These are much more difficult to prepare than manganous salts, the relative stability of the bivalent and tervalent salts being reversed completely on passing from chromium to manganese. The salts which have been isolated belong to two series, in which the manganese is either tervalent or quadrivalent.

(*a*) *Fluorides.*—**Manganic fluoride,** MnF_3, was prepared by Moissan by the action of fluorine on manganous iodide, MnI_2. The **trihydrate,** $MnF_3,3H_2O$, can be obtained in red crystals by dissolving manganese dioxide in hydrofluoric acid; the **double fluoride,** $2KF,MnF_3,H_2O$ or K_2MnF_5,H_2O, is prepared by dissolving manganese dioxide in potassium hydrogen fluoride. A **potassium manganifluoride,** K_2MnF_6 (compare K_2SiF_6), in which manganese is quadrivalent, has been prepared by converting potassium manganate into potassium manganite, K_2MnO_3, by the action of water and carbon dioxide and dissolving it in potassium hydrogen fluoride; the manganifluoride crystallises out in golden, hexagonal tablets, and volatilises when heated, but is decomposed by water, which gives a precipitate of hydrated manganese dioxide.

(*b*) *Chlorides.*—The solution obtained by dissolving manganese dioxide in cold hydrochloric acid gives only double salts of **manganese trichloride** of the type $MnCl_3,2KCl$, the **tetrachloride,** $MnCl_4$, being stable only in ethereal hydrochloric acid at low temperatures. **Potassium manganichloride,** K_2MnCl_6, corresponding with the manganifluoride, K_2MnF_6, has, however, been prepared by boiling potassium permanganate with glacial acetic acid and saturating the solution with hydrochloric acid.

(*c*) *Cyanides.*—Manganese acetate gives with potassium cyanide a green precipitate of the **double cyanide,** $2KCN,MnC_2N_2$, or $K_2MnC_4N_4$, which changes on standing into dark blue crystals of **potassium manganocyanide,** $K_4MnC_6N_6$, compare potassium ferrocyanide, $K_4FeC_6N_6$ (p. 787); on exposure to air this oxidises to **potassium manganicyanide,** $K_3MnC_6N_6$, compare potassium ferricyanide, $K_3FeC_6N_6$, a more stable compound, which can be reduced back to the manganocyanide by the action of potassium amalgam.

(*d*) *Iodate.*—Iodic acid in presence of potassium iodate also converts manganese dioxide into a quadrivalent compound, a violet-brown double salt of the **tetraiodate** having the formula $2KIO_3,Mn(IO_3)_4$.

(*e*) *Sulphate.*—**Manganic sulphate,** $Mn_2(SO_4)_3$, is prepared by dissolving the dioxide in sulphuric acid, from which it separates as a powder. The **alums** of this series have been prepared by dissolving the **triacetate,** $Mn(C_2H_3O_2)_3$, in sulphuric acid in presence of an alkaline sulphate and crystallising out at a low temperature. They are, however, unstable and can only be recrystallised at low temperatures and in the presence of sulphuric acid. The triacetate used in this preparation is made by the action of potassium permanganate on

manganous acetate, and can be purified by recrystallisation from acetic acid.

Manganates and Permanganates.

When manganese dioxide is fused with potassium hydroxide it absorbs oxygen and is converted into **potassium manganate,** K_2MnO_4 :

$$4KOH + 2MnO_2 + O_2 = 2K_2MnO_4 + 2H_2O.$$

By dissolving in water and evaporating in a vacuum, green crystals can be obtained which are isomorphous with potassium sulphate. **Sodium manganate,** $Na_2MnO_4,10H_2O$, prepared in a similar manner, is isomorphous with sodium sulphate, $Na_2SO_4,10H_2O$.

Potassium permanganate, $KMnO_4$, is formed when manganese dioxide is oxidised by heating with potassium chlorate and potassium hydroxide ; it is also formed from the manganate by the action of chlorine,

$$2K_2MnO_4 + Cl_2 = 2KCl + 2KMnO_4,$$

by atmospheric oxidation,

$$4K_2MnO_4 + 2H_2O + O_2 = 4KMnO_4 + 4KOH,$$

or by spontaneous decomposition of the manganate in neutral solution,

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH,$$

since the manganates are only stable in presence of an excess of free alkali. Potassium permanganate separates from water in anhydrous purple prisms with a green metallic lustre. When heated, it gives a mixture of potassium manganate and manganese dioxide,

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2 ;$$

it also changes into the manganate when boiled with a strong solution of potassium hydroxide. It is a powerful oxidising agent, especially in presence of acids ; thus in neutral or alkaline solutions it is reduced to manganese dioxide, liberating three atoms of oxygen from $2KMnO_4$:

$$2KMnO_4 + H_2O = 2MnO_2 + 2KOH + 3O ;$$

but in acid solutions it is reduced to a manganous salt and liberates five atoms of oxygen as shown in the equation

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

It is used as an oxidising agent in the estimation of ferrous salts, p. 792, and also in estimating other oxidising agents such as persulphuric acid ; these are reduced with an excess of ferrous sulphate, and this excess is then titrated against potassium permanganate. More remarkable is its action upon hydrogen peroxide, in which these two powerful oxidising agents reduce one another, molecular oxygen being formed as shown in the equation

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

where five atoms of oxygen are contributed by the permanganate and five atoms by the peroxide.

Sodium permanganate, $NaMnO_4$, resembles potassium permanganate, but is deliquescent and too soluble to be crystallised out readily. **Ammonium permanganate,** $(NH_4)MnO_4$, is isomorphous with potassium permanganate, but explodes when heated rapidly or when struck. **Barium permanganate,** $Ba(MnO_4)_2$, and **silver permanganate,** $AgMnO_4$, are both soluble in water, but the latter only sparingly so.

Permanganic acid, $HMnO_4$, can be prepared by the action of dilute sulphuric acid on barium permanganate ; it is very unstable, liberating oxygen readily, and is a powerful oxidising agent. **Permanganic anhydride,** Mn_2O_7, is formed by the action of sulphuric acid on potassium permanganate as follows. When potassium permanganate is dissolved in cold concentrated sulphuric acid it gives a green solution which appears to contain a **permanganic sulphate,** $(MnO_3)_2SO_4$, since, when common salt is added to the solution, **permanganyl chloride,** MnO_3Cl, distils out as a yellow gas, which condenses to a greenish-brown liquid,

$$MnO_3{\cdot}OK \rightarrow MnO_3{\cdot}OH \rightarrow (MnO_3)_2SO_4 \rightarrow MnO_3{\cdot}Cl.$$

When the sulphate solution is diluted with water, **dimanganese heptoxide,** Mn_2O_7, separates from the solution as an unstable reddish-brown liquid, which does not freeze at $-20°$ and does not vaporise at $60°$; it redissolves in sulphuric acid to form an olive-green liquid, and in water it yields a violet solution which may perhaps contain permanganic acid. When the green solution of potassium permanganate in sulphuric acid is allowed to drip on to anhydrous sodium carbonate, small quantities of **manganese trioxide,** MnO_3, are carried forward by the carbon dioxide as a pink spray, which can be caught on fragments of glass in a **U**-tube cooled by a freezing mixture ; it is decomposed by water as shown in the equation

$$3MnO_3 + H_2O = 2HMnO_4 + MnO_2.$$

Detection and Estimation of Manganese.

Manganese compounds give an amethyst-coloured borax bead in an oxidising flame and a colourless bead in a reducing flame.

Manganous salts give a flesh-coloured precipitate of **manganous sulphide,** MnS, with alkaline sulphides ; this can be separated with zinc sulphide, ZnS, from the black sulphides of nickel and cobalt, by dissolving it in cold dilute hydrochloric acid ; the manganese can then be precipitated as **manganous hydroxide,** $Mn(OH)_2$, by adding an excess of sodium hydroxide, in which zinc hydroxide is soluble, and converted into **sodium manganate,** Na_2MnO_4, by fusing with sodium hydroxide, or it may be precipitated as **manganese dioxide,** MnO_2 aq., by boiling off the sulphuretted hydrogen, oxidising with potassium chlorate, and adding sodium hydroxide. The formation of a green manganate by fusion with an alkali, and of a red permanganate on acidifying the melt, are conclusive tests for the presence of manganese.

Manganates and *permanganates* can be identified both by their colour and by the changes of colour which they undergo on reduction

and reoxidation ; or by reducing them to manganous salts, *e.g.*, by the action of sulphur dioxide, and identifying these by the usual tests.

Manganese is estimated gravimetrically as **trimanganese tetroxide,** Mn_3O_4 (compare cobalt), formed by ignition after precipitating the metal as carbonate, sulphide, or peroxide. It may also be precipitated as phosphate from ammoniacal solution and weighed after ignition of the precipitate as **manganese pyrophosphate,** $Mn_2P_2O_7$.

Manganese is estimated volumetrically by converting it into a permanganate (*e.g.*, by oxidising the solution with nitric acid, lead peroxide, and dilute sulphuric acid) and then titrating against a standard solution of oxalic acid.

Manganese dioxide can be estimated volumetrically by boiling it with hydrochloric acid, passing the chlorine into potassium iodide, and titrating the iodine ; or gravimetrically by determining the loss in weight through liberation of carbon dioxide when oxalic acid is oxidised by manganese dioxide in presence of sulphuric acid,

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O.$$

The atomic weight of manganese has been determined :

(i) By estimating the halogen in manganous chloride and bromide,

$$MnCl_2 : 2Ag. \quad MnBr_2 : 2Ag.$$

(ii) By converting manganous oxide into manganous sulphate and manganous sulphate into manganous sulphide,

$$MnO : MnSO_4 : MnS.$$

(iii) By determining the percentage of silver in silver permanganate,

$$AgMnO_4 : Ag.$$

CHAPTER XLI

IRON, COBALT, AND NICKEL

Atomic number.	*Element.*	*Symbol.*		*Atomic weight.*
26	Iron	Fe	=	55·84
27	Cobalt	Co	=	58·97
28	Nickel	Ni	=	58·68

Occurrence of Iron.

After oxygen (50 per cent.), silicon (26 per cent.), and aluminium (7 per cent.), iron is the most abundant element in the earth's crust, in which it is present to the extent of rather more than 4 per cent. Igneous rocks contain iron in two states of oxidation, namely, $3\frac{1}{2}$ per cent. of FeO and $2\frac{1}{2}$ per cent. of Fe_2O_3, or 6 per cent. in all; but this is only available for metallurgical work when it has been separated from its silica and concentrated in secondary deposits as an iron ore, *e.g.*, as MAGNETITE, Fe_3O_4, HÆMATITE, Fe_2O_3, LIMONITE, Fe_2O_3 aq., or SIDERITE, $FeCO_3$. Iron is also segregated in the form of sulphides, *e.g.*, PYRITES, FeS_2; but sulphur is so objectionable an impurity in iron that these compounds are generally used as ores of sulphur and not of iron.

(*a*) **Ferrous oxide,** FeO, is present in igneous rocks as a **ferrous silicate,** in association with isomorphous magnesium silicates, *e.g.*, as an orthosilicate, $[Mg,Fe]_2SiO_4$, in olivine, and as a metasilicate, $[Mg,Fe]SiO_3$, in hornblende or augite. Under the influence of water and carbon dioxide these compounds give a soluble **ferrous bicarbonate,** $Fe(CO_3H)_2$, which may be carried away and reprecipitated elsewhere. In the presence of organic matter a SPATHIC IRON ORE containing a considerable proportion of SIDERITE or **ferrous ca bonate,** $FeCO_3$, may be formed in this way. In an oxidising atmosphere a **hydrated ferric oxide,** Fe_2O_3 aq., is precipitated as LIMONITE, but this may be converted by heat and pressure into **anhydrous ferric oxide,** Fe_2O_3, or HÆMATITE, or even into MAGNETITE, Fe_3O_4.

(*b*) The **ferric oxide,** Fe_2O_3, of igneous rocks is present as a **ferric silicate,** replacing aluminium in alumino-silicates, such as potash-felspar or orthoclase, $K[Al,Fe]Si_3O_8$. The weathering of these rocks leads to the elimination of alkali and silica, and to an accumulation of

hydrated alumina and ferric oxide, as in the red earthy "laterite," which is abundant in India and may contain more than 50 per cent. of ferric oxide; residual deposits of this kind are important sources of aluminium, but are not usually available as iron ores, unless concentrated by solution and reprecipitation as described under (*a*) above. A **potassium ferric silicate,** $KFeSi_2O_6$, is also found as GLAUCONITE, a remarkable green mineral which appears in oceanic deposits just beyond the limits to which mud is carried by the action of the currents and waves of the shore, and which is the principal form in which potash and iron are precipitated from sea-water.

(*c*) **Ferroso-ferric oxide,** Fe_3O_4, or MAGNETITE (Fig. 267, p. 781), crystallises directly from igneous rocks which are poor in silica: in this form it often carries with it titanium dioxide, TiO_2 (which replaces silica to the extent of 0·8 per cent. in igneous rocks, p. 678), giving rise in extreme cases to the separation of ILMENITE or **ferrous titanate,** $FeTiO_3$. The magnetite of North Sweden is exceptionally free from sulphur and phosphorus and is used in making the very pure "Swedish charcoal iron" (p. 766).

(*d*) **Ferrous sulphide,** FeS, occurs in meteorites as TROILITE. The sulphide which separates directly from igneous rocks as PYRRHOTITE contains a rather larger proportion of sulphur and may consist in part of **ferroso-ferric sulphide,** Fe_3S_4. The **disulphide,** FeS_2, is found as PYRITES in igneous rocks (which must presumably have crystallised under pressure to retain this high proportion of sulphur); it is also widely distributed as cubic crystals of pyrites (Fig. 268, p. 782) and as orthorhombic crystals (Fig. 269) or nodules (Fig. 35, p. 46) of MARCASITE in sedimentary rocks, where the sulphide has probably been precipitated from soluble salts of iron.

Smelting of Iron.

The smelting of iron depends upon the reduction of its oxide-ores with carbon, giving rise to metallic iron and a mixture of carbon monoxide and carbon dioxide, *e.g.*,

$$Fe_2O_3 + 3C = 2Fe + 3CO,$$
$$2Fe_2O_3 + 3C = 4Fe + 3CO_2.$$

These two actions proceed simultaneously, and at the temperature of the furnace there is a definite condition of equilibrium between the two oxides of carbon, corresponding with a ratio of 2 or 3 molecules of carbon monoxide to 1 molecule of carbon dioxide. The reduction is carried out in a BLAST-FURNACE (Fig. 257) consisting of a vertical shaft narrowed towards the top and the bottom and lined with fireclay blocks. Coke is now generally used as fuel, the volatile matter of the coal (including gas, tar, and ammonia) being recovered before using it in the blast-furnace. The maximum size of the furnace depends largely on the hardness of the coke used for reduction; in England the furnaces

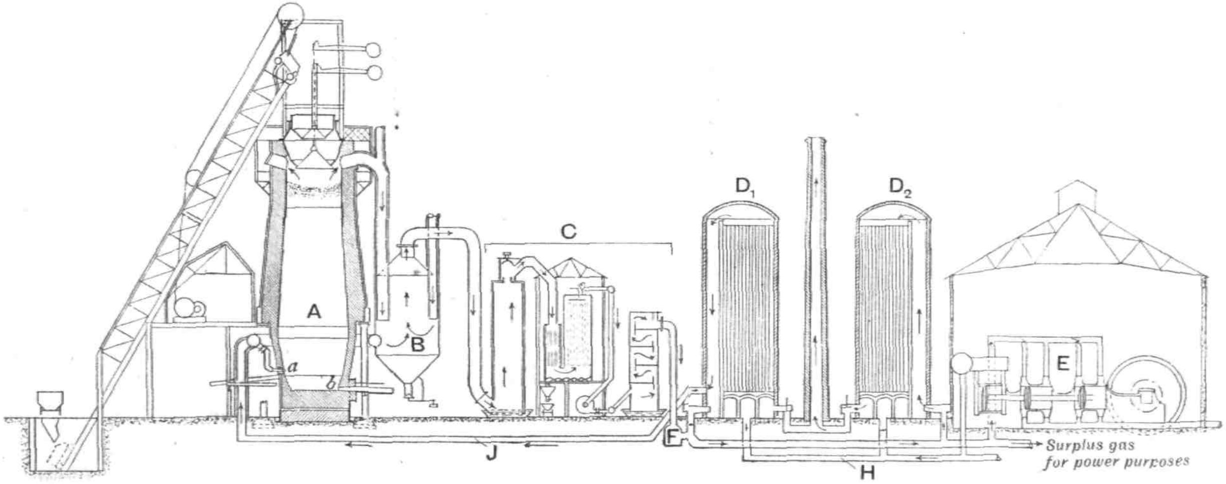


FIG. 257.—DIAGRAM OF BLAST-FURNACE WITH COWPER STOVES, CAPACITY 250 TONS PER DAY (SKINNINGROVE IRON CO.).

A, Mechanically-charged Blast-furnace (*a* = one of the tuyeres, *b* = tapping-hole). *B*, Dust-catcher. *C*, Halberger-Beth Dry Gas-cleaner. *D*, Cowper Stoves (D_1 is heating the blast and being cooled thereby; D_2 is being heated by combustion of Furnace Gas). *E*, Blowing-engine operated by Furnace Gas. *F*, Main Gas-flue from Gas-cleaner to Cowper Stoves, Blowing-engine, etc. *H*, Cold-blast Main, from Blowing-engine to Cowper Stoves; *J*. Hot-blast Main, from Cowper Stoves to Blast-furnace.

are usually about 80 ft. in height and give an output of 500 to 1000 tons of iron per week. The ore and fuel are fed in through a hopper at the top of the furnace and are smelted continuously with the help of a blast of air, which is led into the lower part of the furnace through water-jacketed nozzles known as TUYERES. The ore is reduced to ferrous oxide and then to metal by carbon monoxide in the upper part of the furnace, and then absorbs carbon, melts, and sinks down into the well of the furnace.

When a sufficient quantity of metal has accumulated, it is drawn off and run into channels and moulds, where it solidifies in the form of PIG-IRON. This is a crude form of iron. containing in a typical case about 4 per cent. of carbon, 2 per cent. of silicon, and small quantities of manganese, phosphorus, and sulphur. On account of its low melting-point and ready production it is used in foundry work as CAST IRON for cheap metallic castings. By burning out the non-metallic impurities it is converted into WROUGHT IRON, or MALLEABLE IRON, the purest form of commercial iron, whilst the removal of all but 0·1 to 1·5 per cent. of carbon gives STEEL of various grades.

Slag.

Nearly all iron ores contain substantial quantities of earthy impurities, and especially of clay, which is a typical constituent of the sediments which accompany the deposition of iron ores from solution. As the whole of the materials fed into the blast-furnace are removed in a fluid form, provision must be made for melting the earthy impurities as well as the metallic iron. This is done by adding limestone to the charge; the lime unites with the clay to form a fusible SLAG, consisting mainly of calcium alumino-silicates, but including a small proportion of iron (usually less than 0·5 per cent.) in the form of ferrous silicate. The slag also takes up calcium sulphide, and is therefore of value in removing sulphur from the metal; but practically the whole of the phosphorus of the ore is reduced to a phosphide of iron, Fe_3P, which is retained by the metal instead of passing into the slag. Some slags when quenched in water and ground can be used as cement, and considerable quantities are used as road metal in combination with tar derived from the coke-ovens.

Blast-furnace Gases.

The inflammable gases which escape at the top of the furnace are now made use of in three ways.

(*a*) *Regenerative Heating.*—The hot gases were formerly led through chambers filled with brickwork which became heated by the gases and was then used to heat the air supply to the furnace. This method of producing a HOT BLAST is known as REGENERATIVE HEATING (p. 498). In modern practice the cold clean gas is mixed with air and burnt in

Cowper stoves (Fig. 257) so as to raise its temperature by combustion; the burnt gases heat the brickwork of the stove and escape finally from a chimney.

Two chambers are provided, so that whilst the gases from the furnace are passing through one and making it hot, the air supply to the furnace is passing through the other and withdrawing its heat from it. The quantity of fuel used in a blast furnace depends largely on the difficulty of attaining the high temperature that is needed for melting the iron. The hot blast therefore effects an economy of fuel much greater than would be expected from the number of thermal units carried into the furnace. For the same reason it has been found practicable, especially in the United States, to effect a further marked economy of fuel by using a DRY BLAST, from which the moisture has been removed by cooling to − 5° prior to regenerative heating.

(*b*) *Potash Recovery.* — The solid dust from the blast-furnace contains appreciable quantities of potassium salts, mainly chloride. The proportion of these varies with the nature of the ore and can be increased by adding a little salt to the charge in order to displace the potassium by sodium; but as it is necessary to clean the gases before they can be used for the production of power, the removal of the dust may be advantageous even when the yield of potash is not very high.

(*c*) *Production of Power.*—When cooled and freed from dust, the inflammable gases from the blast-furnace are comparable in value with a poor air-producer gas (p. 467), from which they differ in composition mainly in containing a larger proportion of carbon dioxide. They can therefore be used as a source of heat, or, with the help of gas engines, as a source of power. The power available from this source should be sufficient for all the operations required to convert the iron into steel rails.

Manufacture of Wrought Iron.

The original process for making WROUGHT IRON was by PUDDLING, that is, by working a pasty mass of the metal at a red heat in contact with air. During this process considerable quantities of the magnetic oxide, Fe_3O_4, were formed as "finery cinder" (used by Priestley in many of his experiments), but the carbon, sulphur, and phosphorus were burnt out preferentially, giving rise to a pure iron containing very little impurity except small streaks of slag.

MALLEABLE IRON is now generally made by "boiling" pig-iron in the hearth of a reverberatory furnace lined with oxide of iron (Fig. 258). The iron is here melted completely; the silicon and manganese are oxidised and removed as a slag, which also carries with it most of the phosphorus, after which the liberation of carbon monoxide by interaction of the carbon of the metal with the oxygen of the lining causes the metal to "boil." The removal of the other elements raises the melting-point of the iron, which begins to separate in a solid form. It is collected in lumps and hammered into bars, which are then cut,

hammered, and rolled at a welding temperature to any desired extent, to produce the fibrous structure characteristic of wrought iron. As "dry puddling" is now obsolete, the term "puddling" is now commonly applied to the method of manufacture here described.

The working to which it is subjected gives to this form of iron a fibrous structure and a remarkable degree of toughness, which, coupled with its high tensile strength, rendered it very suitable for tie-rods and for building ships and bridges. It has now been replaced very largely by steel, produced at a lower cost and of greater strength for an equal weight of metal; but it is still used for rivets, for blacksmiths' work, or where welding is required. Wrought iron has also been used during a very long period of time for making the purest grades of steel. The pure Swedish iron used for making steel for cutlery is, however,

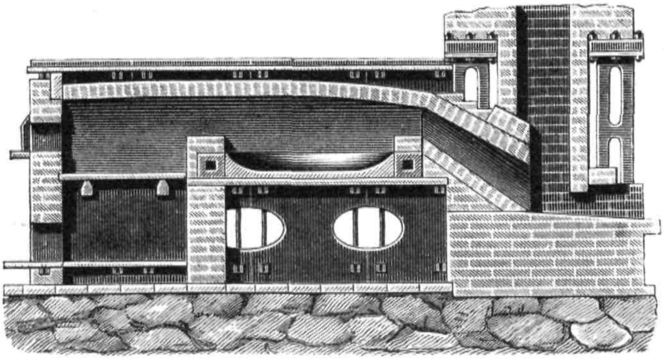


FIG. 258.—FURNACE FOR MAKING MALLEABLE IRON.

made on a hearth in which the surface of the molten metal is exposed to a blast of air, and is not worked like a true wrought iron.

Manufacture of Steel.

The manufacture of steel demands not only a reduction in the amount of carbon and the removal of most of the silicon in pig-iron, but also a very thorough purification from sulphur and phosphorus, which make the metal brittle; it is, therefore, usual to specify a maximum of, say, 0·05 per cent. of sulphur and 0·05 per cent. of phosphorus. Sulphur can be removed or neutralised in part in a preliminary purification by the addition to molten iron of manganese, which forms a sulphide, MnS, of high melting-point, and only sparingly soluble in the metal; but phosphorus, if present in the pig-iron, must usually be eliminated by using a special process of manufacture.

The term steel was originally applied to alloys containing from 0·5 to 1·5 per cent. of carbon, which could be hardened and tempered by heat treatment (p. 772); the term has now been extended,

however, to include MILD STEEL, containing 0·1 to 0·5 per cent. of carbon, which differs from wrought iron in having been made by melting instead of by working in a plastic condition.

(*a*) *By Cementation.*—One of the earliest methods for manufacturing steel consisted in heating bars of wrought iron with charcoal. During the process of CEMENTATION, which lasts for about eleven days, carbon is absorbed and the wrought iron is thereby converted into steel. The product, known as BLISTER STEEL, is usually converted into SHEAR STEEL, as used in making cutlery, by forging it under a steam-hammer. The highest grades of tool-steel are melted in crucibles after cementation and are known as CRUCIBLE STEEL. An analogous process in which the surface only of the metal is carbonised is known as CASE-HARDENING; this process was used extensively at one time for hardening the surface of armour-plate, whilst retaining the original toughness of the back of the plate, and is still used largely in the motor industry and in making machinery.

(*b*) *The Bessemer Process.*—In the Bessemer process, cast iron was converted into steel by blowing air through it until practically all the silicon and carbon had been burnt out. The product was then converted into steel by the addition of SPIEGELEISEN, *i.e.*, of iron containing a high proportion of manganese and carbon.

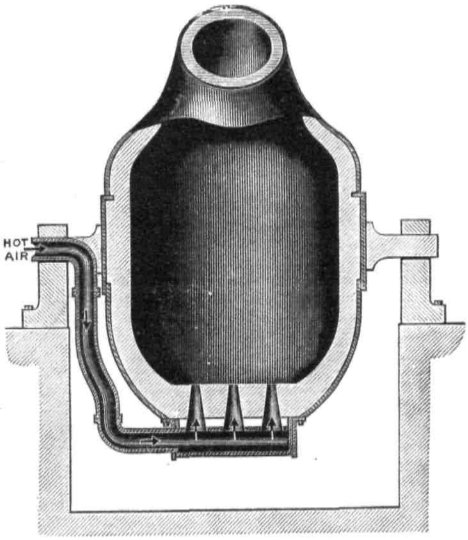


FIG. 259.—BESSEMER CONVERTER.

The BESSEMER CONVERTER (Fig. 259) is a domed vessel with a fixed hood, mounted on trunnions so that it can be tilted, and provided with an air-chamber in the base from which air can be blown through holes in the lining. Molten metal was poured into the converter, whilst tilted into a horizontal position, with the mouth directed upwards so as to keep the air-holes clear. The air-blast was then turned on and the converter brought back to the vertical position so that the air burnt out first the silicon and then the carbon, the combustion of the silicon producing so much heat that the iron became hotter during the process, and remained molten in spite of its higher freezing-point.

The Bessemer converter was at first provided with an acid lining consisting mainly of silica, and the process could only be applied successfully for making

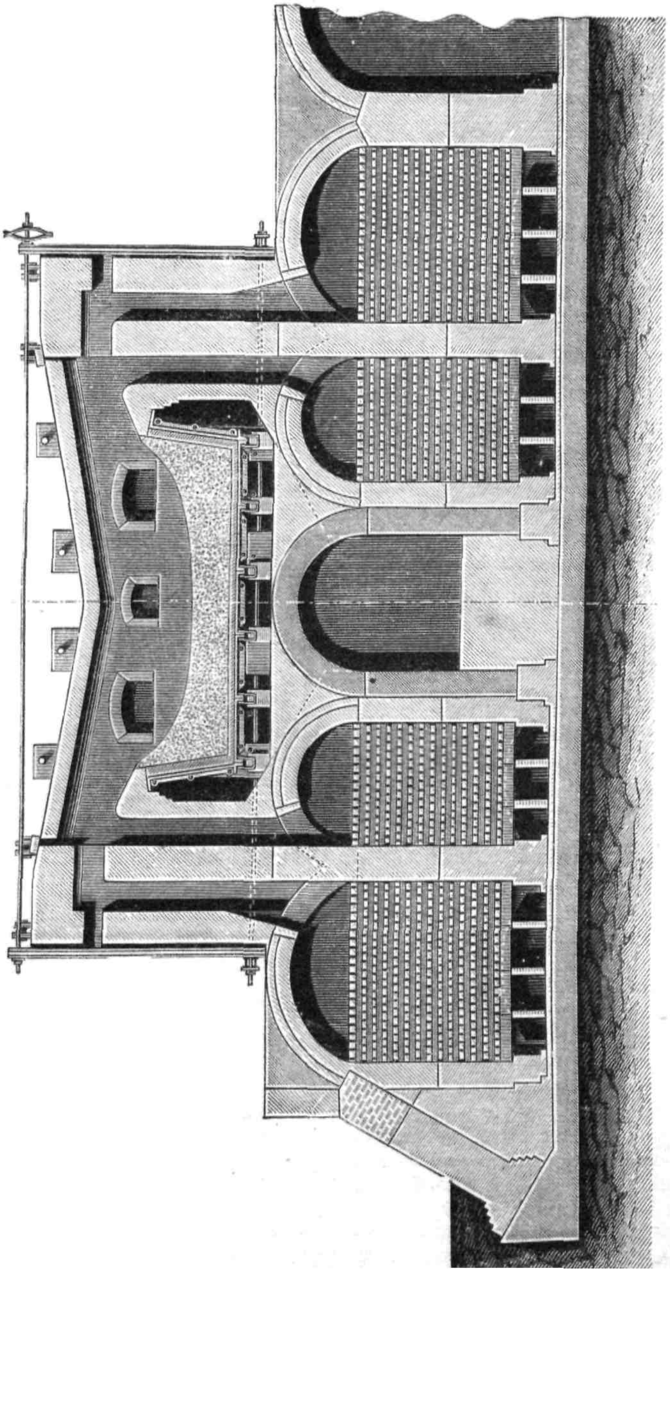


FIG. 260.—OPEN-HEARTH FURNACE.

ACID STEEL from iron that contained but little phosphorus. This difficulty was overcome in the THOMAS AND GILCHRIST PROCESS by making use of a BASIC LINING of lime and magnesia (prepared by calcining dolomite), and a slag containing lime, which absorbs the phosphorus in the form of calcium phosphate. This process was of particular value in enabling use to be made of the MINETTE ORES of Lorraine, on which the iron industry of the Rhine Valley is based. The iron used in making BASIC STEEL by this process must contain very little silicon and sulphur, but phosphorus up to 3 per cent. is an actual advantage, since the heat of combustion contributes to maintain the temperature of the charge. The phosphorus of BASIC SLAG is of remarkable value as a fertiliser for poor pasture land, giving rise to a strong growth of clover and a great improvement in the food value of the herbage.

(c) *The Siemens-Martin Process*.—The Bessemer converter has now been superseded very largely by an OPEN-HEARTH FURNACE (Fig. 260), heated regeneratively by producer gas to a temperature above the melting-point of wrought iron. Pig-iron, steel scrap, and iron ore are melted together in the hearth in such proportions as to eliminate the greater part of the carbon in combination with the oxygen of the ore. The process can be used either with an acid lining, if the iron is free from phosphorus, or with a basic lining when phosphorus is present; in the latter case, lime is added to produce a basic slag. If the iron contains more than an average amount of sulphur, fluorspar is added to maintain the fluidity of the slag, whilst using a high proportion of lime to absorb the sulphur.

(d) *Manufacture of Special Steels*.—The manufacture of special steels depends on the addition to the charge in the hearth or in a crucible of elements such as silicon, manganese, tungsten, and chromium. These are usually added in the form of alloys with iron, prepared if necessary in the electric furnace; nickel is, however, added as a metal and not as an alloy. The electric furnace is also used for the preparation of special steels: electric furnaces in which the metal in a circular trough is heated by an "induced current" flowing through it have the advantage that the metal does not come into contact with carbon, so that its composition can be controlled with great exactness.

The Four Forms of Iron.

Pure iron is a grey crystalline metal of density 7·8; it melts at 1530° and boils in an electric furnace at 2450°. The metal is tetramorphous; thus, when cooled from a high temperature, a change of state accompanied by a liberation of latent heat takes place at 1400°, at 895°, and again at 766°. Fig. 261 shows the resulting excess of temperature of iron over platinum, when cooling together in the same furnace. The four modifications of iron are distinguished as: α-Iron, stable up to 766°; β-Iron, stable from 766° to 895°; γ-Iron, stable from 895° to 1400°; δ-Iron, stable from 1400° to the melting-point.

(*a*) **α-Iron,** or FERRITE, is a soft, tough metal, and is the principal constituent of wrought iron. It is diamagnetic, *i.e.*, it attracts to itself the lines of magnetic force, and possesses a high coefficient of magnetisation, which makes it of unique value in the construction of electro-magnets and transformers. These exceptional magnetic qualities disappear when the iron passes from the α to the β state at 766° (Fig. 262).

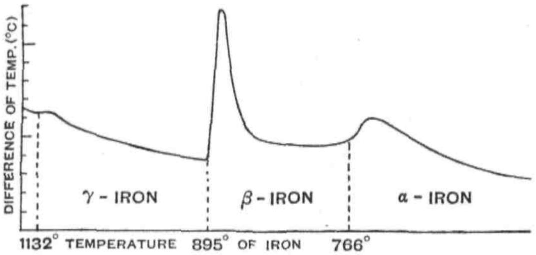


FIG. 261.—LIBERATION OF HEAT DURING COOLING OF IRON.

(*b*) **β-Iron** is not very important, as it exists only within a very narrow range of temperature and composition. It is denser than α-iron, so that there is a slight contraction when iron is heated through the transition-point at 766°; there is also a small absorption of heat, but the outlines of the crystals, which are constructed like those of α-iron on a centred cubic lattice (p. 220), are not altered.

(*c*) γ-**Iron** is stable from 896° to 1400°, and is there-ore the form in which the metal usually crystallises from its alloys. It differs from α- and β-iron in that it forms solid solutions with carbon, which is retained by the crystals up to a maximum of 1·9 per cent. The change from β- to γ-iron is accompanied by a large absorption of heat, but by no marked change of volume. γ-Iron resembles β-iron in being devoid of the special magnetic properties of α-iron, but differs from α- and β-iron in being constructed on a face-centred cubic lattice, like copper (p. 214).

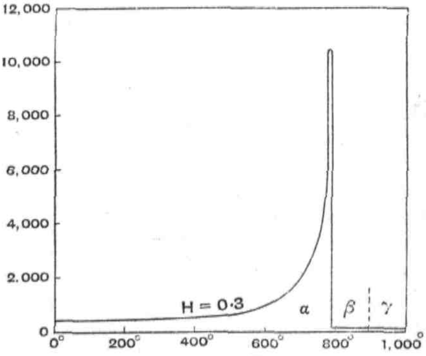


FIG. 262.—INFLUENCE OF TEMPERATURE ON MAGNETIC PERMEABILITY OF IRON.

Influence of Carbon on Iron.

The properties of iron are influenced in a very remarkable way by small proportions of carbon, which may be present

(i) In solution in the liquid.
(ii) In solid solution in crystals ot γ-iron.
(iii) In combination as a carbide, Fe_3C.
(iv) In the free state as graphite

Some of the principal effects produced by this element are set out in the following paragraphs.

(*a*) *Freezing-point of Cast Iron.*—The freezing-point of iron is lowered by the addition of carbon (Fig. 263), just as the freezing-point of water is lowered by the addition of salt (Fig. 72); but the effects produced are much more remarkable, since 1 per cent. of carbon produces a fall of nearly 100° in the freezing-point of iron. Thus, whilst pure iron freezes at 1530°, the eutectic alloy of iron and carbon, containing 4·3 per cent. of carbon, freezes at about 1150°. This is the lowest temperature to which the freezing-point of iron can be reduced by means of carbon. The freezing-point can, however, also be lowered by other elements, although the effects are smaller; thus, 10 per cent. of silicon is required to lower the freezing-point of iron by 100°, as contrasted with 1·2 per cent. in the case of carbon.

(*b*) *Grey and White Cast Iron.*—The carbon in cast iron may crystallise out in an uncombined state as GRAPHITE, or in combination with iron as CEMENTITE or **carbide of iron,** Fe_3C. In contrast with graphite, which is the softest constituent of cast iron, cementite is one of the hardest. It is more soluble than graphite and tends to crystallise out from the melt at a lower temperature (Fig. 263). It is also less stable than graphite, and on prolonged annealing at 900° or above breaks down as shown in the equation

$$Fe_3C = 3Fe + C;$$

this decomposition takes place much more readily when silicon is also present. Cast iron containing a high proportion of silicon is therefore soft, and grey in colour, on account of the graphite which it contains, and is known as GREY CAST IRON. Cast iron in which most of the carbon is present in the combined form is harder and whiter than grey cast iron, and is distinguished as WHITE CAST IRON. The influence of silicon on the condition of the carbon may be shown in two extreme cases as follows:

	Si	C (as graphite).	C (as carbide).
White cast iron ..	0·9	0·1	3·0 per cent.
Grey cast iron ..	3·5	3·3	0·1 ,,

Most samples of cast iron are intermediate between these in the proportion of silicon which they contain, and in the distribution of the carbon between the alternative forms of graphite and cementite.

(*c*) *Quenched Steel.*—The iron which separates from a melt containing carbon is not pure γ-iron, but may contain up to 1·9 per cent. of carbon in solid solution, probably in the form of a carbide. These solid solutions are completely stable only at high temperatures, but unlike pure iron they can be fixed more or less completely in the γ-form by quenching with water, provided that they contain a sufficient proportion of carbon or of some other isomorphous element; when found as a constituent of QUENCHED STEEL they are described as AUSTENITE.

The unchanged solid solutions are not specially hard, but tend to break up into iron and carbide, and become very hard during the initial stages of this change; the first product of change, consisting of interlacing crystals, is known as MARTENSITE, and is a typical constituent of steels which have been hardened by quenching.

(*d*) *Crystallisation of Iron and Carbon from Solid Solution.*—The solid solutions of carbon in γ-iron behave in many respects just like liquid solutions. Thus (i) the *solubility of carbon in solid γ-iron* diminishes progressively from 1·9 per cent. at 1150° to 0·9 per cent. at 690°. Alloys containing more than 0·9 per cent. of carbon therefore deposit carbon, not only during the solidification of the melt, but also in cooling through the range of temperatures from 1150° to 690°. These solid solutions usually deposit the excess of carbon in the form of cementite, Fe_3C, just as molten iron which is rich in carbon but poor in silicon deposits cementite during solidification. On the other hand, (ii) solid solutions which are poor in carbon and rich in iron deposit β-iron and α-iron on cooling, just as molten iron deposits γ-iron in the form of austenite. Finally (iii) the solid solutions form an EUTECTOID ALLOY which contains 0·9 per cent. of carbon and from which α-iron and carbide of iron crystallise out together from solid solution at a constant temperature of 690°, just as molten iron and carbon give an eutectic alloy which contains 4·3 per cent. of carbon and crystallises out at 1150°.

(*e*) *Recalescence.*—A sample of steel containing 0·9 per cent. of carbon in solid solution as AUSTENITE passes directly at 690° into the fine-grained eutectoid alloy of ferrite (*i.e.*, α-iron) and cementite, Fe_3C, to which the name of PEARLITE is given on account of its pearly lustre. This change involves a direct conversion in one operation of γ- into α-iron, as well as a complete segregation of the carbon as carbide, and is accompanied by a considerable liberation of latent heat. When, therefore, a carbon-steel has been overcooled below 690° to a point at which it has ceased to glow, the formation of pearlite is sometimes accompanied by a rise of temperature which causes the metal to glow up again, giving rise to the phenomenon of RECALESCENCE.

(*f*) *Tempered Steel.*—The tempering of steel depends on taking a quenched steel, in which most of the carbon has been fixed in solid solution by sudden cooling, and heating it cautiously, so as to produce a carefully-controlled conversion of the solid solution into ferrite and cementite, thereby diminishing the hardness of the metal but increasing its toughness. The product is a TEMPERED STEEL, the hardness of which diminishes as the duration and the temperature of heating are increased. The progress of tempering can be followed conveniently by watching the slow oxidation of the surface when the metal is tempered in contact with air; this produces a film of oxide the colour of which changes from yellow to blue as its thickness increases; the pale yellow colour produced by heating to 220–230° is suitable for tempering cutting tools,

whilst the full blue produced by heating nearly to 300° is used in tempering springs. The complete conversion of austenite into pearlite includes two intermediate stages, thus :

AUSTENITE → MARTENSITE → SORBITE → PEARLITE.*

The original solid solution can only be preserved, as austenite, by quenching, when other elements (*e.g.*, manganese) are present in addition to carbon. Martensite represents the first stage in the segregation of iron and carbon, as it is seen in very hard quenched steels, and consists of interlacing crystals. Tempered steels consist mainly of sorbite, a fine-grained mixture of ferrite and cementite, in which the banded structure of pearlite, which is characteristic of annealed steels, is not yet fully developed.

(*g*) *Malleable Cast Iron.*—The carbon in cast iron may separate

(i) As primary carbon directly from t he liquid ;
(ii) As secondary carbon, crystallising out from solid solutions between 1150° and 690° ;
(iii) As a constituent of pearlite crystallising at 690°.

The primary carbon can be obtained in the form of graphite by slow cooling, but the secondary carbon usually separates as cementite, and this is also the form in which the carbon is always present in pearlite. By heating an iron casting with oxide of iron to a red heat for about two days it is possible in some instances to burn out a part of the carbon (by a reversal of the process of cementation) and to convert the remainder into soft graphite which is known as TEMPER CARBON. The casting, which then contains nothing but ferrite and graphite, is soft and malleable like wrought iron, although it differs from wrought iron in that it cannot be welded readily.

Equilibrium-diagram for Iron and Carbon.

The effects produced by the addition of carbon to iron are shown diagrammatically in Fig. 263. The principal features of this diagram are :

(*a*) *A* V*-shaped freezing-point curve showing the crystallisation of iron and carbon from the liquid alloy.*

(i) The crystallisation of *iron* in the form of austenite is shown on the left. These crystals are not pure iron, but contain in solid solution a proportion of carbon amounting to nearly one-half of that in the liquid from which the crystals have separated.

(ii) The separation of *graphite* is shown on the right by a full line, intersecting the austenite curve, at 4·3 per cent. of carbon and 1150°, the eutectic-point of this series of alloys.

* It has been suggested that martensite consists of twin-crystals of austenite and that sorbite represents an early stage in the segregation of pearlite, in which the two components are still so finely divided as to be almost colloidal in character.

(iii) The separation of carbon in a metastable form as cementite, Fe_3C, is shown on the right by a broken line below the line for graphite.

(b) A V-shaped diagram showing the crystallisation of iron and carbon from solid solution.

(i) On the left the crystallisation of β-iron and α-iron is shown by two intersecting lines; solid solutions containing from 0 to 0·4 per cent. of carbon deposit β-iron in the range from 895° to 766°, whilst α-iron is deposited directly from solid solutions containing from 0·4 to 0·9 per cent. of carbon at temperatures from 766° to 690°.

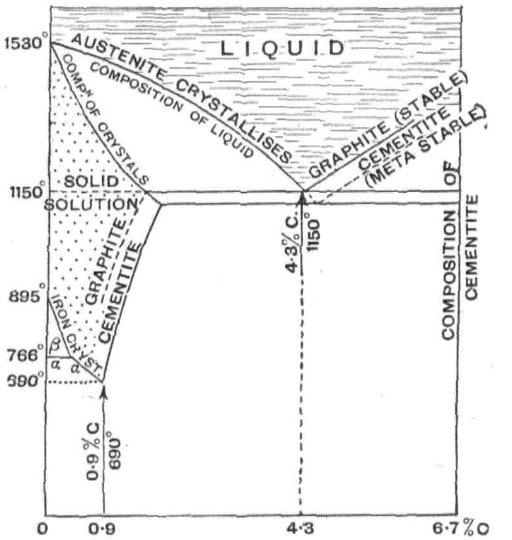


FIG. 263.—EQUILIBRIUM-DIAGRAM FOR IRON AND CARBON.

(ii) On the right hand a full line shows the crystallisation of cementite from solid solutions containing from 0·9 to 1·9 per cent. of carbon. The crystallisation of graphite is shown only by a broken line, since although it is more stable than cementite, it is difficult to get the carbon to separate in this form.

(iii) The eutectoid-point of the solid solution at 0·9 per cent. of carbon and 690° has already been described as the "recalescence-point" of steel.

Special Steels.

As in the case of aluminium (p. 655), and of copper (p. 832), most of the useful alloys of iron consist of or contain *solid solutions*, although cast iron is a fusible *eutectic alloy*, and the harder steels usually contain *chemical compounds*, such as the carbide Fe_3C, either in solid solution or in a free state; but as pure iron is twice as strong as copper and four times as strong as aluminium, many of its solid solutions have a very high tensile strength, which renders them of unique value in industry.

The usefulness of carbon in steel is limited by the fact that γ-iron at the eutectic temperature of 1150° will *only* take up 1·9 per cent. of this element in solid solution, diminishing to 0·9 per cent. at the eutectoid temperature of 690°, which is the lowest temperature at

which γ-iron can be rendered stable by means of carbon. This limitation does not occur in the case of elements such as manganese and nickel, which will form solid solutions in all proportions with γ-iron (Fig. 265), but not with α-iron; by making use of metals such as these, therefore, the temperature at which γ-iron passes into the magnetic α-form can be lowered to any desired extent, giving rise to alloys which are permanently non-magnetic. Even these alloys, however, appear to owe their hardness mainly to carbon, since the solid solutions are not usually hard, but become hard only during the initial stages of separation of carbon from them. Hardness appears, indeed, to depend on some condition of strain, so that a pure metal in a condition of stable equilibrium is usually softer than when strained mechanically, or by the presence of foreign elements.

In making SPECIAL STEELS a large number of elements are used, including Si, Mn, Cr, Ni, W, V, Mo. These are selected, not only on account of the way in which they form solid solutions, and thereby influence the transition-temperatures of the different forms of iron, but also according to the physical and mechanical qualities which they develop in the alloy.

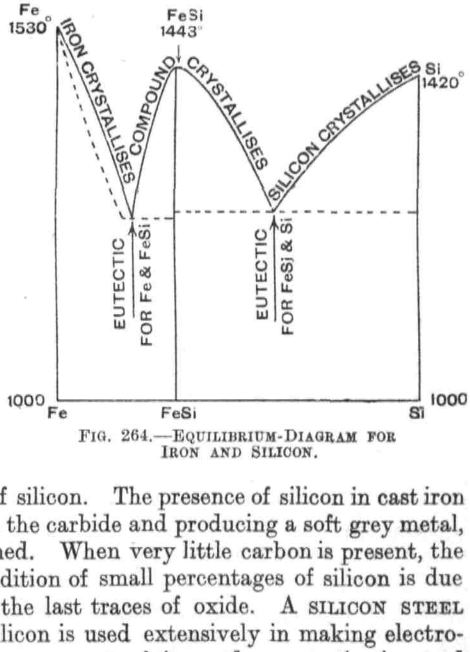


FIG. 264.—EQUILIBRIUM-DIAGRAM FOR IRON AND SILICON.

(*a*) *Silicon Steel.*—Silicon combines with iron to form the compounds Fe_2Si and FeSi (Fig. 264), but like carbon it also forms solid solutions in γ-iron, up to a maximum of 18 per cent. of silicon. The presence of silicon in cast iron has the effect of breaking up the carbide and producing a soft grey metal, which is very easily machined. When very little carbon is present, the softening of iron by the addition of small percentages of silicon is due mainly to the removal of the last traces of oxide. A SILICON STEEL containing 4 per cent. of silicon is used extensively in making electro-magnets and transformers on account of its ready magnetisation and demagnetisation.

(*b*) *Manganese Steel.*—Manganese is particularly effective in preserving the γ-form of iron. It is therefore used for making non-magnetic steels; but its principal value is in the manufacture of very tough steels which are capable of resisting wear, as in the pinions of dredger buckets, in tramway points and crossovers, and in grinding and crushing machinery, where excessive wear is expected. Alloys of this character

are also used for steel helmets and light armour. An alloy containing 12 per cent. of manganese and 1 per cent. of carbon shows a remarkable combination of strength and toughness, namely, a tensile strength of about 70 tons per square inch, with an extension of more than 60 per cent. before fracture (Fig. 202, p. 524); but it is so tough that it cannot be planed or drilled except with a grindstone or blow-pipe.

(*c*) *Chromium Steel.*—A similar alloy containing 12 per cent. of chromium and 0·3 per cent. of carbon is used as STAINLESS STEEL for cutlery. The temperature to which the metal must be heated in order to get the carbon into solid solution in γ-iron is raised by the addition of chromium, so that this form of steel must be quenched from a higher

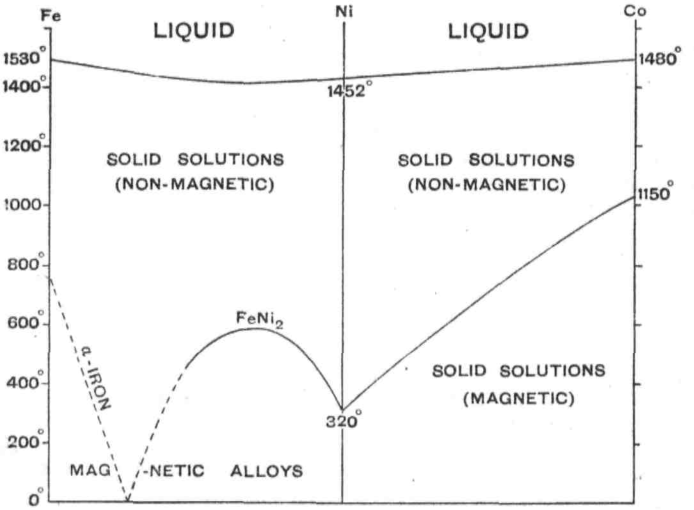


FIG. 265.—EQUILIBRIUM-DIAGRAMS FOR IRON, NICKEL, AND COBALT.

temperature than carbon steel in order to harden it sufficiently to produce a permanent cutting-edge.

(*d*) *Nickel Steels.*—At high temperatures, nickel forms a complete series of solid solutions with iron; but these break up on cooling, giving either a-iron or a compound, $FeNi_2$, the separation of which from the solid solution is shown clearly in Fig. 265. For comparison the equilibrium-diagram for nickel and cobalt is shown, since here the magnetic as well as the non-magnetic forms of the two metals form solid solutions in all proportions.

Nickel steels are remarkable for their toughness and have been used for making armour-plate. Alloys containing about 25 per cent. of nickel are non-magnetic. They also possess the remarkable property of being almost entirely free from thermal expansion over a considerable range of temperatures; such alloys, under the name of INVAR, are used

for secondary standards of length, for surveying tapes, for pendulum-rods, and for dividing-engines, where constancy of length is particularly important. In some of these alloys the elasticity of the metal also remains stationary or even increases instead of diminishing with rising temperature; such alloys can be used with great advantage for the hair-springs of watches, not merely to avoid the diminution of elasticity of the spring which usually results from rise of temperature, but also to compensate for the retardation caused by the expansion of the balance-wheel. These peculiarities of the nickel steels are explained by supposing that the contraction which takes place when α-iron passes into β-iron at 766°, and the increase of elasticity which accompanies the conversion of β-iron into γ-iron at 895°, are in these alloys brought down to atmospheric temperatures and used to neutralise the ordinary effects of rise of temperature on the physical properties of the metal.

(e) *Self-hardening steels* or high-speed tool-steels are alloys of iron with tungsten, chromium, and other elements, *e.g.*,

W 12–18, Cr 2–6, C 0·5 to 0·6, V 0·3 to 0·5 per cent.,

which possess the property of retaining their hardness instead of softening when heated to 700°, *e.g.*, by heavy work in a lathe. Tools made from these alloys do not soften even when the cutting-edge becomes red-hot, and can therefore be run at a far higher speed than when a simple carbon steel is used. The effect of carbon in retarding the conversion of γ into α iron has already been described (p. 771); the special properties of the self-hardening steels appear to be due at least in part to the still greater difficulty of effecting this change in a solid solution which contains not merely two, but four or five, isomorphous constituents.

Compounds of Iron.

Chemical Properties of Iron.

(a) *Valency.*—Iron forms two principal series of salts, namely,

(i) Bivalent *ferrous salts* derived from the oxide, FeO.
(ii) Tervalent *ferric salts* derived from the oxide, Fe_2O_3.

The ferrous salts are more readily prepared than the corresponding chromous salts derived from the oxide, CrO; but they differ from the bivalent salts of manganese, nickel, and cobalt in the fact that they are oxidised to the tervalent ferric salts on exposure to air. Compounds of higher valency corresponding with chromic acid and the chromates have been prepared but are not of any technical importance. The ferrous salts are usually green in colour, at least when hydrated, whilst the ferric salts are yellow; but ferrous oxalate, FeC_2O_4, is yellow, potassium ferric oxalate, $K_3Fe(C_2O_4)_3$, and potassium ferric silicate, $KFeSi_2O_6$, are green, and anhydrous ferric chloride is black.

(*b*) *Combination with Non-metals.*

(i) *Carbon* unites directly with iron to form the **carbide,** Fe_3C, and frequently crystallises out from the metal in this form; this "combined carbon" yields volatile hydrocarbons when the metal containing it is dissolved in acids, whereas "free carbon" or graphite remains as an insoluble black residue.

(ii) *Sulphur* unites directly with iron to form the fusible **ferrous sulphide,** FeS, in addition to compounds containing a larger proportion of sulphur.

(iii) *Phosphorus* forms a fusible **phosphide,** Fe_3P, by direct combination with iron.

(iv) *Silicon* unites with iron to form the **silicides,** FeSi (Fig. 264) and Fe_2Si.

(v) Iron burns in *oxygen*, and is oxidised by steam at a red heat, forming the magnetic oxide, Fe_3O_4; it also unites directly with the *halogens*.

(vi) Iron does not unite with *hydrogen*, although it is permeable to this gas.

(vii) *Nitrogen* does not combine directly with iron, but a **nitride,** Fe_2N, is formed by the action of ammonia on the metal.

(*c*) *Combination with Carbon Monoxide.*—Iron combines with carbon monoxide to form metallic CARBONYLS. **Iron pentacarbonyl,** FeC_5O_5, is a yellow liquid boiling at 103°, and forming yellow crystals at − 21°. It is decomposed by light according to the equation

$$2FeC_5O_5 = Fe_2C_9O_9 + CO.$$

The golden crystals produced in this way decompose at 100° according to the equation

$$Fe_2C_9O_9 = FeC_5O_5 + 4CO + Fe;$$

but when heated in solution in toluene, in an atmosphere of carbon dioxide at 95°, they give green crystals of an **iron tetracarbonyl,** $(FeC_4O_4)_n$,

$$Fe_2C_9O_9 = FeC_4O_4 + FeC_5O_5;$$

this is decomposed into iron and carbon monoxide by heating to 140°.

(*d*) *Oxidation.*—Iron is oxidised not only by oxygen, but also by steam and by carbon dioxide, when a balanced action is set up, leading to a condition of equilibrium between steam and hydrogen in the one case, and between carbon dioxide and carbon monoxide in the other.

$$Fe + H_2O \rightleftharpoons FeO + H_2$$
$$Fe + CO_2 \rightleftharpoons FeO + CO.$$

(i) The equilibrium between the two oxides of carbon in presence of iron and ferrous oxide is represented by the equation

$$Fe + CO_2 \rightleftharpoons FeO + CO - 1960 \text{ calories.}$$

The heat-change shown in this equation is very small and the ratio of the two oxides of carbon is therefore (in accordance with Nernst's Theorem, p. 258) almost independent of the temperature, thus:

TABLE 88.—REDUCTION OF CARBON DIOXIDE BY IRON.

$$Fe + CO_2 \rightleftharpoons CO + FeO.$$

	CO_2	CO	
At 950°	23%	77%	
At 900°	25	75	*i.e.*, $CO_2 : CO = 1 : 3$ approximately
At 750°	30·6	69·4	
At 600°	33·4	66·5	*i.e.*, $CO_2 : CO = 1 : 2$ approximately

(ii) In the interaction of iron with water-vapour two stages of oxidation can be recognised, each corresponding with a definite ratio of water-vapour to hydrogen, thus:

TABLE 89.—REDUCTION OF STEAM BY IRON.

$$\text{I.}\quad Fe + H_2O\ (\text{steam}) \rightleftharpoons FeO + H_2 + 8{,}000\ \text{calories}$$
$$\text{II.}\quad 3Fe + 4H_2O\ (\text{steam}) \rightleftharpoons Fe_3O_4 + 4H_2 + 15{,}000\ \text{calories}$$

		I.	II.
At 400°	H_2O/H_2 =	0·15 or 1 : 7	0·20 or 1 : 5
At 600°	H_2O/H_2 =	0·33 or 1 : 3	0·52 or 1 : 2
At 800°	H_2O/H_2 =	0·61 or 3 : 5	1·35 or 4 : 3.

The oxidation of the iron is exothermic at each stage, and the proportion of hydrogen produced therefore decreases as the temperature rises.

(*e*) *The Rusting of Iron.*—Iron dissolves in dilute acids, including carbonic acid, which gives ferrous bicarbonate and hydrogen,

$$Fe + 2H_2CO_3 = Fe(CO_3H)_2 + H_2.$$

The RUSTING OF IRON depends on the oxidation of ferrous bicarbonate to ferric hydroxide,

$$4Fe(CO_3H)_2 + O_2 + 2H_2O = 4Fe(OH)_3 + 8CO_2.$$

This is a weak base which does not form a carbonate and therefore liberates the carbon dioxide for further attack on the metal. Zinc, which forms only bivalent salts, and aluminium, which forms only tervalent salts, do not rust in the same way as iron, although they have a higher heat of oxidation (p. 657).

(*f*) *Passive Iron.*—Although iron dissolves readily in dilute acids, *e.g.*,

$$Fe + H_2SO_4 = FeSO_4 + H_2,$$

strong nitric acid renders the metal PASSIVE, *i.e.*, it becomes resistant to attack even by weaker acids. The nature of the change which takes place at the surface of the metal is not certain (although it has been suggested that a resistant film of oxide may be formed), but the

effect of this treatment is to give to iron some of the peculiar chemical properties of aluminium.

Iron and Oxygen.

Iron forms three principal oxides, namely,

Ferrous oxide, FeO	Ferroso-ferric oxide, or
Ferric oxide, Fe_2O_3	ferrous ferrite, Fe_3O_4.

(*a*) **Ferrous oxide,** FeO, is not found in the free state, although enormous quantities are present in igneous rocks in combination with silica, usually mixed with magnesia in ferro-magnesian minerals. It can be prepared by oxidising iron with nitrous oxide at 200°, or by partial reduction of ferric oxide by hydrogen at 300°. It burns in air with incandescence, and also absorbs carbon dioxide readily, forming ferrous carbonate. **Ferrous hydroxide,** $Fe(OH)_2$, is precipitated from ferrous solutions by the addition of an alkali,

$$FeSO_4 + 2NaOH = Fe(OH)_2 + Na_2SO_4.$$

It is colourless when pure, but readily turns green, and finally yellow by conversion to ferric hydroxide. It is a much stronger base than ferric hydroxide, since it forms a carbonate, $FeCO_3$, and a bicarbonate, $Fe(CO_3H)_2$, and a very stable sulphide, FeS; moreover, unlike ferric hydroxide, it is not precipitated completely from its salts by a mixture of ammonia and ammonium chloride.

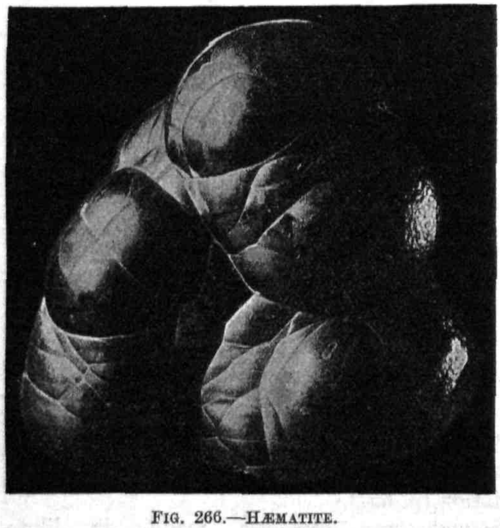


FIG. 266.—HÆMATITE.
(British Museum, Natural History.)

(*b*) **Ferric oxide,** Fe_2O_3, as HÆMATITE (Fig. 266), is an important ore. It is a heavy mineral, of density 5·2, and is isomorphous with corundum, Al_2O_3, although it is only rarely found in a crystalline form; as in the case of magnetite, the crystals are opaque and have a slight metallic conductivity (p. 527). The massive mineral is brownish-red in colour, gives a red streak on paper, and is used as a pigment under the name of RED OCHRE; ferric oxide prepared by heating ferrous sulphate is known as "colcothar"

or ROUGE. Hydrated forms of ferric oxide are found, *e.g.*, as LIMONITE, to which the formula $2Fe_2O_3,3H_2O$ is sometimes given; but the only crystalline mineral hydrate is GÖTHITE, which has the composition $HFeO_2$, compare diaspore, $HAlO_2$. Limonite has probably been formed by the action of oxygen on ferrous bicarbonate, and is therefore substantially identical with iron rust; it gives a yellow streak on paper and is used as a pigment under the name of YELLOW OCHRE. Like rust, it often contains unoxidised ferrous carbonate.

Ferric hydroxide, $Fe(OH)_3$, is a very weak base, which can be precipitated from its salts by ammonia, by caustic alkalies, or by carbonates, compare $Al(OH)_3$; it differs from aluminium hydroxide in that it does not dissolve in an excess of caustic alkali, although it is present as the acid constituent in many spinels, *e.g.*, $Mg[Al,Fe]_2O_4$.

(*c*) **Ferroso-ferric oxide,** or **magnetic oxide of iron,** Fe_3O_4, is the most stable oxide of iron. It is formed as SMITHY SCALE OT FINERY CINDER when iron is heated in air, and also when iron is oxidised by steam as in Lavoisier's experiments (p. 86); it is also an important mineral under the name of MAGNETITE (Fig. 267).

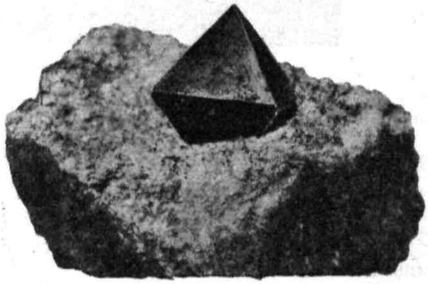


FIG. 267.—MAGNETITE.
(British Museum, Natural History.)

It is a bluish-black compound, opaque, and with a semi-metallic lustre like graphite; its density, 5·2, agrees very closely with that of hæmatite and of iron pyrites. It has a slight metallic conductivity and is used as an electrode for arc lights, and in electrolysis as an anode which is not attacked by oxygen or chlorine. It melts at about 1535°, *i.e.*, rather above the melting-point of iron and just below the melting-point of palladium.

The oxide crystallises unchanged from igneous rocks which are poor in silica, and can be used as a solvent to promote the recrystallisation of silicates such as albite, $NaAlSi_3O_8$. As magnetite, it forms cubic crystals isomorphous with the spinels, *e.g.*, $MgAl_2O_4$; it may therefore be regarded as a spinel in which magnesium has been replaced by ferrous iron and aluminium by ferric iron, giving rise to a "ferrous ferrite" analogous to magnesium aluminate. Its chemical properties are those of a loose compound of ferric and ferrous oxides, with a heat of formation from these oxides of about 8,000 calories.

(*d*) Higher oxides of iron corresponding with the disulphide, FeS_2, or with chromic acid, CrO_3, are not known, but **sodium ferrate,** Na_2FeO_4, and **potassium ferrate,** K_2FeO_4, compare K_2CrO_4, have been prepared by fusing ferric oxide with an alkaline hydroxide and nitrate, and these have been converted by double decomposition into **barium ferrate,** $BaFeO_4$.

Iron and Sulphur.

Ferrous sulphide, FeS, is found in meteorites as TROILITE, and is prepared artificially by direct combination of iron with sulphur or by precipitating a ferrous salt with a soluble sulphide, *e.g.*,

$$FeSO_4 + Na_2S = FeS + Na_2SO_4.$$

It melts readily and can be cast into rods or sticks, which are black in colour and have a semi-metallic lustre. It is decomposed by acids and

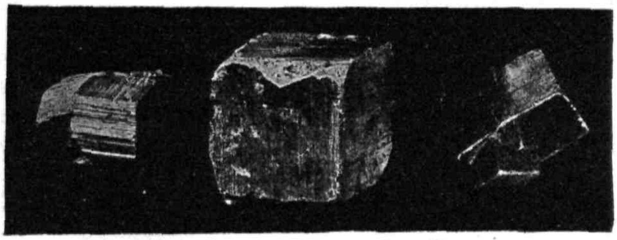


FIG. 268.—STRIATED CUBES OF IRON PYRITES.

is commonly used for the preparation of sulphuretted hydrogen, *e.g.*,

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

It oxidises in moist air to ferrous sulphate and combines readily with sulphur, forming the disulphide, FeS_2.

Ferroso-ferric sulphide, Fe_3S_4 (?), is formed when iron pyrites is distilled.

$$3FeS_2 = Fe_3S_4 + S_2.$$

The variable composition of the product, which is present in igneous rocks as PYRRHOTITE or MAGNETIC PYRITES, is attributed to isomorphism.

Ferric sulphide, Fe_2S_3, can be prepared from iron and sulphur or by pouring a solution of a ferric salt into an excess of ammonium sulphide. It is of importance chiefly in combination with other sulphides, *e.g.*, copper pyrites, $CuFeS_2$, is regarded as a cuprous ferric sulphide, Cu_2S,Fe_2S_3; the simple salts $KFeS_2$ and $NaFeS_2,2H_2O$ have also been prepared.

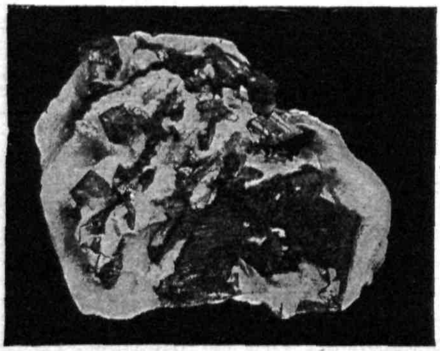


FIG. 269.—ARROWHEAD CRYSTALS OF MARCASITE. (British Museum, Natural History.)

Iron disulphide, FeS_2, is dimorphous. IRON PYRITES (Fig. 268) and MARCASITE (Fig. 269) may be regarded as the parent substances of two

series of isomorphous compounds, in which iron is replaced by manganese, cobalt, or nickel, and sulphur by arsenic or antimony.

Cubic Series.	*Orthorhombic Series.*
Pyrites, FeS_2	Marcasite, FeS_2
Cobaltite, CoSAs	Mispickel, FeSAs
Also MnS_2,NiSAs,NiSSb, $CoAs_2$,$NiAs_2$,$PtAs_2$	Also CoSAs,NiSAs, $FeAs_2$,$CoAs_2$,$NiAs_2$.

The disulphide is formed readily by direct combination of ferrous sulphide with sulphur; acid solutions containing free sulphuretted hydrogen tend to give marcasite, whilst high temperature and alkalinity favour the formation of pyrites. Marcasite is a metastable form of the disulphide and passes into pyrites with liberation of heat when heated to 450°; it is less dense than pyrites (4·9 as compared with 5·0) and behaves differently towards some chemical agents. Marcasite oxidises readily to ferrous sulphate and probably provided the material from which oil of vitriol was first prepared.

Reduction and Oxidation of Salts of Iron.

When iron is dissolved in dilute acids ferrous salts are produced, *e.g.*,

$$Fe + 2HCl = FeCl_2 + H_2$$
$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

They can also be produced by reduction of ferric salts, *e.g.*, by zinc or magnesium in presence of sulphuric acid,

$$Fe_2(SO_4)_3 + Mg = 2FeSO_4 + MgSO_4$$
$$Fe_2(SO_4)_3 + Zn = 2FeSO_4 + ZnSO_4,$$

or by stannous chloride or titanous chloride,

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$
$$FeCl_3 + TiCl_3 = FeCl_2 + TiCl_4.$$

The reduction is accompanied by a marked change of colour, since the ferric salts give deep yellow solutions, whilst the green ferrous salts appear almost colourless; the end of the reduction can also be detected by using potassium ferrocyanide as an external indicator, since this gives a precipitate of Prussian blue with ferric, but not with ferrous salts.

The converse process of oxidation takes place on exposure to air, giving clear solutions when free acid is present, but insoluble basic ferric salts when neutral solutions are used.

$$4FeSO_4 + 2H_2SO_4 + O_2 = 2Fe_2(SO_4)_3 + 2H_2O.$$

Oxidation can also be effected quantitatively by titrating with oxidising agents such as potassium permanganate or potassium dichromate,

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$
$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = 2KCr(SO_4)_2 + 3Fe_2(SO_4)_3 + 7H_2O;$$

in the former case no indicator is needed beyond the colour of the permanganate, but in the latter case potassium ferricyanide (which gives a blue precipitate with ferrous salts but only a brown colour with ferric salts) is used as an external indicator.

Ferrous Salts.

Ferrous chloride, $FeCl_2$, sublimes in colourless crystals when iron is heated in a current of hydrogen chloride or ferric chloride in a current of hydrogen.

$$Fe + 2HCl = FeCl_2 + H_2$$
$$2FeCl_3 + H_2 = 2FeCl_2 + 2HCl.$$

Its vapour density of 1500° corresponds with the formula $FeCl_2$. It dissolves readily in water, from which it separates as the **tetrahydrate,** $FeCl_2,4H_2O$; aqueous solutions can also be prepared by dissolving iron in hydrochloric acid. The anhydrous chloride also combines with ammonia to form the compound $FeCl_2,6NH_3$, but this does not behave as a co-ordinated compound (p. 797) since it is decomposed by water and gives the normal reactions of ferrous salts, of chlorides, and of ammonia.

Ferrous sulphate or GREEN VITRIOL, $FeSO_4,7H_2O$, is formed by the weathering of marcasite,

$$2FeS_2 + 2H_2O + 7O_2 = 2FeSO_4 + 2H_2SO_4,$$

or by dissolving iron in dilute sulphuric acid. It crystallises with seven molecules of water, but also forms a **pentahydrate,** $FeSO_4,5H_2O$, which is isomorphous with $CuSO_4,5H_2O$, and is a common impurity in the latter; hydrates with $4H_2O$, $3H_2O$, and $2H_2O$ have also been described. The **heptahydrate,** $FeSO_4,7H_2O$, can be purified by precipitating it from a strong solution in water by the addition of alcohol; the double salt, **ferrous ammonium sulphate,** $FeSO_4,(NH_4)_2SO_4,6H_2O$, or $(NH_4)_2Fe(SO_4)_2,6H_2O$, is, however, usually preferred in analytical work, its solubility being only about a quarter of that of the simple sulphate. Unlike the isomorphous sulphates of Mn, Co, Ni, Cu, and Zn, ferrous sulphate oxidises readily on exposure to air, and can be used as a reducing agent to precipitate gold from solution or for the estimation of oxidising compounds such as the persulphuric acids (p. 350),

$$2FeSO_4 + H_2SO_5 = Fe_2(SO_4)_3 + H_2O.$$

Ferrous sulphate also possesses the power of combining with nitric oxide, forming a brown compound, probably $2FeSO_4,NO$, as in the "brown-ring test" for nitrates (p. 406); it can therefore be used for purifying nitric oxide, since this can be separated again from the brown solution by warming.

When heated, ferrous sulphate decomposes, giving off a mixture of

sulphur dioxide and sulphur trioxide and leaving a residue of ferric oxide or COLCOTHAR,

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$

Ferrous sulphate is used as the principal source of ferrous compounds, *e.g.*, in making ink and Prussian blue; it is also used in dyeing and in tanning.

Ferrous nitrate, $Fe(NO_3)_2,6H_2O$, cannot be prepared by dissolving iron in nitric acid on account of the oxidising action of nitric acid on ferrous salts; it has been prepared in a crystalline form by dissolving ferrous sulphide in nitric acid or by double decomposition from barium nitrate and ferrous sulphate.

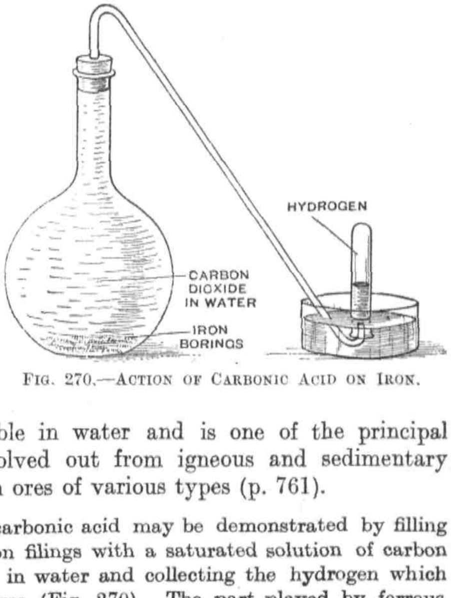


FIG. 270.—ACTION OF CARBONIC ACID ON IRON.

Ferrous carbonate, $FeCO_3$, occurs as SPATHIC IRON ORE and is also present in rust and in clay ironstone; crystalline ferrous carbonate is found as SIDERITE, $FeCO_3$ (p. 630). **Ferrous bicarbonate,** $Fe(CO_3H)_2$, like calcium bicarbonate, is soluble in water and is one of the principal forms in which iron is dissolved out from igneous and sedimentary rocks and redeposited as iron ores of various types (p. 761).

The solubility of iron in carbonic acid may be demonstrated by filling up a flask containing some iron filings with a saturated solution of carbon dioxide in water and collecting the hydrogen which is set free (Fig. 270). The part played by ferrous bicarbonate in the rusting of iron (p. 779) may be shown by filling the lower part of a beaker with iron nails, covering with a filter-paper, and filling up with water (Fig. 271); iron rust is then formed, by precipitation from solution, on the *upper* surface of the filter-paper.

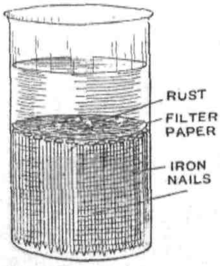


FIG. 271.—RUSTING OF IRON.

Ferrous Silicates.—Ferrous metasilicate, $FeSiO_3$, is present as an isomorphous mixture with $MgSiO_3$ in hornblende and augite; **ferrous orthosilicate,** Fe_2SiO_4, occurs in a similar manner in olivine.

Ferric Salts.

Ferric chloride, $FeCl_3$, sublimes in black scales when chlorine is passed over red-hot iron. It melts at 300° and vaporises readily;

its vapour density at 448° corresponds with the formula Fe_2Cl_6, but diminishes at higher temperatures, perhaps as a result of dissociation into ferrous chloride and chlorine,

$$Fe_2Cl_6 \rightleftharpoons 2FeCl_2 + Cl_2.$$

Ferric chloride dissolves readily in water and can be prepared by dissolving ferric oxide in hydrochloric acid or by dissolving iron in hydrochloric acid and converting the ferrous chloride into ferric chloride by means of chlorine. The aqueous solution is yellow and tends to deposit ferric hydroxide as a result of the hydrolysis of the chloride. Ferric chloride forms a series of yellow hydrates, which resemble those of sulphuric acid in melting at different temperatures (Fig. 272) instead of passing into a lower hydrate when heated, *e.g.*,

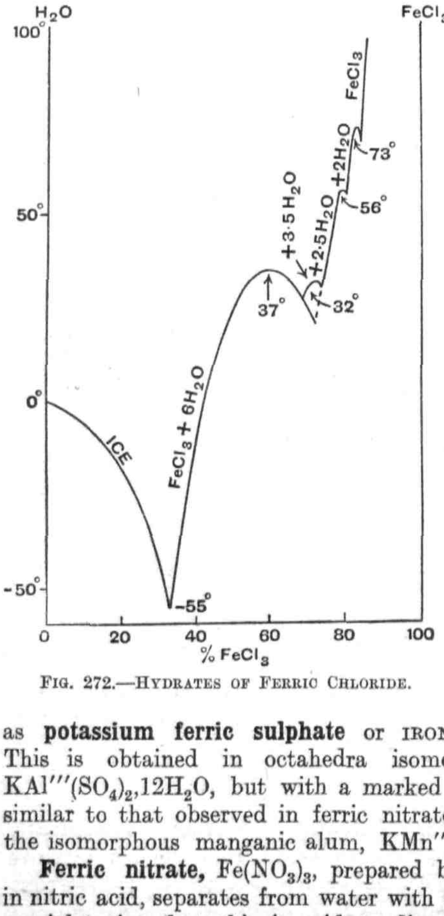


FIG. 272.—HYDRATES OF FERRIC CHLORIDE.

	Melting-point.
$FeCl_3,6H_2O$.	37°
$FeCl_3,3\frac{1}{2}H_2O$.	32·5°
$FeCl_3,2\frac{1}{2}H_2O$.	56°
$FeCl_3,2H_2O$.	73·5°

Ferric chloride is the principal source from which other ferric compounds are prepared.

Ferric sulphate, $Fe_2(SO_4)_3$, like aluminium sulphate, is commonly prepared in the form of a double salt, *e.g.*, as **potassium ferric sulphate** or IRON ALUM, $KFe'''(SO_4)_2,12H_2O$. This is obtained in octahedra isomorphous with potash alum, $KAl'''(SO_4)_2,12H_2O$, but with a marked violet tint; this tint is very similar to that observed in ferric nitrate but is probably not due to the isomorphous manganic alum, $KMn'''(SO_4)_2,12H_2O$.

Ferric nitrate, $Fe(NO_3)_3$, prepared by dissolving iron or its oxide in nitric acid, separates from water with $6H_2O$ or $9H_2O$; it has usually a violet tint, but this is said to disappear when the compound is free from manganese. It is used as a mordant in dyeing.

Ferric phosphate, $FePO_4$, is a constituent of phosphatic rocks when formed by the action of soluble phosphates on materials rich in iron, instead of on limestone.

Potassium ferric disilicate, $KFeSi_2O_6$, or GLAUCONITE, is an important and characteristic deposit in the bed of the ocean. Ferric silicates are also very common as isomorphous mixtures with the corresponding aluminium silicates in minerals such as felspar, $KAlSi_3O_8$, nephelite, $[Na,K]AlSiO_4$, etc.

CYANOGEN COMPOUNDS.

Potassium Ferrocyanide and its Derivatives.

The FERROCYANIDES are an important series of double salts formed by the combination of ferrous cyanide with four equivalents of another cyanide, *e.g.*,

$$FeC_2N_2 + 4KCN = K_4FeC_6N_6,$$

but they are so stable that they are conveniently regarded as metallic salts of hydroferrocyanic acid, $H_4FeC_6N_6$ (see *e* below).

(*a*) *Preparation from Nitrogenous Waste.*—Cyanides were formerly prepared by heating charred nitrogenous organic matter in a reverberatory furnace with molten potash and iron turnings; after solidification, the product was digested and finally extracted with hot water. Potassium cyanide is first formed, probably by the action of ammonia on carbon in presence of potassium carbonate (p. 477),

$$K_2CO_3 + 4C + 2NH_3 = 2KCN + 3CO + 3H_2,$$

and can be separated as such by extracting with alcohol; but when the product is digested with water the cyanide interacts with ferrous sulphide to form **potassium ferrocyanide,** $K_4FeC_6N_6$, a salt which is only moderately soluble in cold water and which crystallises much more readily than the cyanide,

$$6KCN + FeS = K_4FeC_6N_6 + K_2S.$$

(*b*) *Preparation from Spent Iron Oxide.*—A considerable proportion of the volatile nitrogen of coal is liberated as prussic acid or hydrogen cyanide, HCN (p. 478). This is swept forward by the gas along with ammonia and sulphuretted hydrogen; some of it is absorbed by water in the "scrubbers" and appears as an impurity in the "ammoniacal liquor," which frequently contains ammonium cyanide, $NH_4 \cdot CN$; but the acid is so weak that most of it passes through the water and is absorbed with the sulphuretted hydrogen by oxide of iron in the "purifiers." This oxide (when regenerated by exposure to air and moisture, and returned to the purifier) contains sulphur, ferrous hydroxide, and ferric hydroxide; the sulphur converts some of the cyanide into sulphocyanide,

$$HCN + S = HCNS.$$

whilst the ferrous and ferric hydroxides are converted into cyanides and fixed as Prussian blue (see below).

$$Fe(OH)_2 + 2HCN = FeC_2N_2 + 2H_2O$$
$$Fe(OH)_3 + 3HCN = FeC_3N_3 + 3H_2O$$
$$3FeC_2N_2 + 4FeC_3N_3 = \underset{\text{Prussian blue}}{Fe_7C_{18}N_{18}}.$$

In order to recover the cyanides, the spent oxide is washed to remove soluble ammonium salts and mixed with lime in order to convert the Prussian blue into **calcium ferrocyanide,** $Ca_2FeC_6N_6,12H_2O$; this is extracted with cold water and converted into potassium ferrocyanide, either by the direct action of potassium carbonate,

$$Ca_2FeC_6N_6 + 2K_2CO_3 = 2CaCO_3 + K_4FeC_6N_6,$$

or by first precipitating **calcium potassium ferrocyanide,** $CaK_2FeC_6N_6$, by the addition of potassium chloride (which is less expensive than the carbonate), and then removing the rest of the calcium with potassium carbonate:

$$Ca_2FeC_6N_6 + 2KCl = CaCl_2 + CaK_2FeC_6N_6$$
$$CaK_2FeC_6N_6 + K_2CO_3 = CaCO_3 + K_4FeC_6N_6.$$

In another process, **calcium ammonium ferrocyanide,** $Ca(NH_4)_2FeC_6N_6$, is crystallised out instead of the usual calcium ferrocyanide.

(c) *Preparation from Coal-gas.*—The cyanides and sulphides can also be removed from coal-gas by washing with a solution of ferrous sulphate before absorbing the ammonia, thus giving an ammoniacal liquor free from both these impurities. The principal products are ammonium cyanide and ferrous sulphide, which interact to form **ammonium ferrocyanide,** $(NH_4)_4FeC_6N_6$,

$$6NH_4{\cdot}CN + FeS = (NH_4)_4FeC_6N_6 + (NH_4)_2S$$

(compare the conversion of potassium cyanide into potassium ferrocyanide). This is precipitated as **ferrous ferrocyanide,** $Fe_2FeC_6N_6$, by the excess of ferrous sulphate, and the ferrocyanide is recovered in the form of the calcium salt, by adding lime to the sludge as already described.

(d) *Properties of Potassium Ferrocyanide.*—Potassium ferrocyanide dissolves in three times its weight of water at 20° and separates from solution in yellow crystals of the **trihydrate,** $K_4FeC_6N_6,3H_2O$, which are described in commerce as "yellow prussiate of potash." They lose their water at 100°, leaving the anhydrous salt as a colourless powder which ignites readily when heated in air.

Potassium ferrocyanide is one of the most stable DOUBLE SALTS that is known, since it gives none of the ordinary reactions of iron, and can usually be detected only when the cyanogen has been destroyed. Thus when heated it gives carbide of iron and nitrogen,

$$K_4FeC_6N_6 = 4KCN + FeC_2 + N_2,$$

and with strong sulphuric acid it gives potassium, ferrous, and ammonium sulphates and carbon monoxide,

$$K_4FeC_6N_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO.$$

Iron can, however, be displaced by metallic sodium without destroying the cyanide,

$$K_4FeC_6N_6 + 2Na = 4KCN + 2NaCN + Fe,$$

giving a mixture of potassium and sodium cyanides which contains more cyanogen than pure potassium cyanide and is sold as containing up to 109 per cent. of KCN. The iron can also be released by the action of a mercuric salt, which removes the cyanogen in the form of mercuric cyanide, a compound which is almost completely undissociated in water and therefore yields even fewer cyanogen ions than the ferrocyanides,

$$K_4FeC_6N_6 + 3HgCl_2 = 3HgC_2N_2 + 4KCl + FeCl_2.$$

In the presence of light, alkaline sulphides slowly precipitate ferrous sulphide, and oxygen slowly precipitates ferric oxide, perhaps as a result of a slow decomposition of the cyanide.

With soluble cupric salts potassium ferrocyanide gives a brown amorphous precipitate of **cupric ferrocyanide,** $Cu_2FeC_6N_6$; this has been used in experiments on osmotic pressure to provide a "semi-permeable membrane" (p. 171) through which water will pass but not sugar. With ferric salts a precipitate of Prussian blue is formed (p. 790).

(*e*) *Hydroferrocyanic Acid.*—By adding hydrochloric acid to a saturated solution of potassium ferrocyanide, **hydroferrocyanic acid,** $H_4FeC_6N_6$, is set free and can be precipitated by the addition of ether. It crystallises in colourless scales, which are quite stable in dry air at atmospheric temperatures, but turn blue in moist air, probably by oxidation to Prussian blue. In the absence of ether, it dissolves readily in water; when a solution in air-free water is heated to 60° it decomposes into hydrogen cyanide and ferrous cyanide,

$$H_4FeC_6N_6 = 4HCN + FeC_2N_2.$$

Alternatively it has been stated that when the solution is boiled the acid loses half its hydrogen cyanide and gives **ferrous dihydrogen ferrocyanide,**

$$2H_4Fe''C_6N_6 = 6HCN + Fe''H_2(Fe''C_6N_6).$$

In the same way, when potassium ferrocyanide is distilled with dilute sulphuric acid, half of the hydrogen cyanide is set free, the remainder being converted into **ferrous potassium ferrocyanide,** or EVERITT'S SALT, $FeK_2FeC_6N_6$,

$$2K_4FeC_6N_6 + 3H_2SO_4 = 6HCN + 3K_2SO_4 + Fe''K_2(FeC_6N_6).$$

Potassium Ferricyanide.

This salt, which contains ferric instead of ferrous iron,

$$3KCN + FeC_3N_3 = K_3FeC_6N_6,$$

is prepared by the action of chlorine on potassium ferrocyanide,

$$2K_4FeC_6N_6 + Cl_2 = 2K_3FeC_6N_6 + 2KCl.$$

It separates from water in an anhydrous form in deep red crystals, and is known commercially as "red prussiate of potash."

Potassium ferricyanide is less stable than the ferrocyanide and on exposure to light is partly reconverted into this compound. It can therefore be used as an oxidising agent, especially in presence of alkalies. It is also a convenient agent for the detection of ferrous salts, with which it gives a precipitate of Prussian blue, whilst with ferric salts only a brown coloration is produced.

Prussian Blue.

The replacement of potassium by iron in the ferrocyanides and ferricyanides gives rise to a series of cyanides of iron, of which the most important is known as Prussian blue.

Ferrous ferrocyanide, $Fe_2''(Fe''C_6N_6)$, is formed as a colourless precipitate on adding one molecular proportion of potassium ferrocyanide to two molecular proportions of a ferrous salt; on exposure to air it oxidises readily to ferric ferrocyanide or Prussian blue, and is stated to give one of the best of the commercial blues. By using only one molecular proportion of ferrous sulphate, a **ferrous potassium ferrocyanide,** $K_2Fe''(FeC_6N_6)$, is produced which is isomeric with "Everitt's salt" described above.

Ferric potassium ferrocyanide or SOLUBLE PRUSSIAN BLUE, $KFe'''(FeC_6N_6)$, is formed by mixing molecular proportions of potassium ferrocyanide and a ferric salt or of potassium ferricyanide and a ferrous salt,

$$K_4Fe''C_6N_6 + Fe'''Cl_3 = 3KCl + KFe'''(Fe''C_6N_6)$$
$$K_3Fe'''C_6N_6 + Fe''Cl_2 = 2KCl + KFe'''(Fe''C_6N_6).$$

It is a stable compound, and contains the characteristic grouping of a univalent with a tervalent metal which is already familiar in the alums, $KAl(SO_4)_2,12H_2O$, in glauconite, $KFeSi_2O_6$, and in aluminosilicates such as $NaAlSiO_4$, $KAlSi_2O_6$, and $KAlSi_3O_8$. An isomeric compound is formed by oxidising ferrous potassium ferrocyanide.

Ferric ferrocyanide or PRUSSIAN BLUE, $Fe_4'''(Fe''C_6N_6)_3,10H_2O$, or $Fe_7C_{18}N_{18},10H_2O$, which is formed by the further action of ferric chloride on the ferric potassium salt, is one of the most important commercial pigments. A similar, or perhaps identical, substance is produced (under the name of TURNBULL'S BLUE) by the addition of an excess of a ferrous salt to potassium ferricyanide.

Carbonyl and Nitroso-derivatives.

(*a*) *Carbonyl Compounds.*—By the action of carbon monoxide on a boiling solution of potassium ferrocyanide a molecule of potassium cyanide is displaced as shown in the equation

$$K_4FeC_6N_6 + CO = K_3Fe(CO)C_5N_5 + KCN.$$

The products are **potassium carbonyl-ferrocyanide,**

$$K_3Fe(CO)C_5N_5,4H_2O,$$

with potassium formate, H·CO·OK, and ammonia as products of hydrolysis of the potassium cyanide.

This substance is a co-ordinated compound, $K_3[Fe''.CO.5CN]$, in which one of the CN groups of the FeC_6N_6 radical of potassium ferrocyanide, $K_4[Fe''.6CN]$, has been replaced by CO, thereby releasing one of the four atoms of potassium. The compounds of this series, which are quite stable, include a colourless crystalline **carbonyl ferrocyanic acid,** $H_3Fe(CO)C_5N_5$, a purple **ferric salt,** $Fe'''Fe''(CO)C_5N_5$, analogous to Prussian blue, and an apple-green **copper salt** corresponding with the brown ferrocyanide. Salts of this type are present in the crude ferrocyanides prepared from coal-gas, and can be separated by taking advantage of their solubility in alcohol.

(*b*) *Nitroprussides.*—A similar change takes place by the action of nitric oxide on potassium ferrocyanide or ferricyanide in acid solutions,

$$K_3FeC_6N_6 + NO = K_2Fe'''(NO)C_5N_5 + KCN.$$

The product is a **potassium nitrosoferricyanide,** $K_2[Fe'''.NO.5CN]$, in which again one of the CN groups of the FeC_6N_6 radical of the ferricyanide, $K_3[Fe'''.6CN]$, has been displaced by a neutral radical, thereby releasing one atom of potassium. It is a dark red soluble salt, which was described in 1849 as **potassium nitroprusside,** since it was first obtained by the action of nitric acid on potassium ferrocyanide or "yellow prussiate" of potash.

Sodium nitroprusside, $Na_2Fe(NO)C_5N_5,2H_2O$, is less soluble than the potassium salt, and crystallises out first when the compound is prepared by the interaction of ferrous sulphate with potassium cyanide and sodium nitrite. Its principal interest arises from the intense purple colour which it gives with an alkaline sulphide, thus providing a very delicate test for traces of hydrogen sulphide; the development of the colour is probably due to the association of the alkaline sulphide with the NO group, but the nature of the coloured compound has not been established.

Nitroprussic acid is unstable, but has been prepared in dark red needles.

Detection and Estimation of Iron.

Ferric iron is precipitated as **ferric hydroxide,** $Fe(OH)_3$, by the action of ammonia, even in presence of ammonium chloride; ferrous

salts give with ammonia or potassium hydroxide a green precipitate of **ferrous hydroxide,** $Fe(OH)_2$, which becomes brown on exposure to air. Soluble ferrous salts give soluble and insoluble **Prussian blue** on the addition of potassium ferricyanide, whilst ferric salts behave in the same way with potassium ferrocyanide. Ferric salts can also be distinguished by the red colour of **ferric sulphocyanide,** $Fe(CNS)_3$, which is developed on adding a solution of potassium sulphocyanide. A borax bead is coloured dark green by ferrous salts in a reducing flame, and yellow or brown by ferric salts or when oxidation takes place in the bead.

Iron is estimated gravimetrically by precipitation with ammonia as **ferric hydroxide,** $Fe(OH)_3$, if necessary after oxidising ferrous to ferric salts with nitric acid; the hydroxide is ignited and weighed as **ferric oxide,** Fe_2O_3. Aluminium, if present, is separated by dissolving its hydroxide in caustic potash.

The volumetric estimation of iron usually depends on oxidising ferrous to ferric iron (i) by means of potassium permanganate, when no indicator is required,

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O,$$

or (ii) by means of potassium dichromate,

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = 2KCr(SO_4)_2 + 3Fe_2(SO_4)_3 + 7H_2O,$$

using potassium ferricyanide as an external indicator to detect the final disappearance of ferrous iron. The second method is used when chlorides are present, since hydrochloric acid is oxidised by potassium permanganate. The reduction to the ferrous state is effected in the first case by means of zinc and sulphuric acid. In the second case, the ferric salt is reduced by the action of stannous chloride in presence of an excess of hydrochloric acid,

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4,$$

when the completion of the reduction is marked by the disappearance of the strong yellow colour of the solution; the slight excess of stannous chloride is then removed by adding mercuric chloride. By using titanous trichloride, $TiCl_3$, instead of stannous chloride, it is possible to estimate ferric iron by direct titration,

$$FeCl_3 + TiCl_3 = FeCl_2 + TiCl_4.$$

The atomic weight of iron has been determined by reducing ferric oxide to metal, and by converting the metal into ferric oxide in order to give the ratio $Fe_2O_3 : 2Fe$; and also by determining the ratios $FeBr_2 : 2AgBr : 2Ag$.

27. COBALT. Co = 58·97.

Iron, Cobalt, and Nickel.

Although the atomic weight of cobalt is greater than that of nickel, all its chemical properties indicate that the proper place for this element is between iron and nickel and not between nickel and copper. Thus, whilst nickel resembles copper and zinc in giving a bivalent sulphate and no tervalent salts, cobalt resembles iron in forming an important series of tervalent cobaltic salts corresponding with the ferric salts, an unstable potassium cobaltocyanide, $K_4CoC_6N_6$, corresponding with potassium ferrocyanide, and a very stable series of cobalticyanides, *e.g.*, $K_3CoC_6N_6$, corresponding with the ferricyanides, for which no analogy exists in the case of nickel. It may also be noted that the oxide of cobalt which is stable at the highest temperatures is Co_3O_4, compare Fe_3O_4, whereas in the case of nickel strong heating gives only the monoxide, NiO, compare CuO and ZnO.

This arrangement of the elements is confirmed by a study of the high frequency spectra which are emitted when these elements are used as the anticathode of an *X*-ray tube, Fig. 203, p. 536; these spectra show a regular progression in the frequency of the *X*-rays, corresponding with successive atomic numbers, *e.g.*,

24 Cr 25 Mn 26 Fe 27 Co 28 Ni 29 Cu 30 Zn.

As there is no reason to suspect the atomic weights of serious errors, the conclusion is drawn that the atomic weights of cobalt and nickel, like those of argon and potassium, and of tellurium and iodine, are not in the order of their atomic numbers, nor in the order indicated by their chemical properties as expressed in the periodic classification of the elements.

Occurrence of Cobalt.

Cobalt is distributed very widely, *e.g.*, in meteoric iron and in sulphide and arsenide ores, but in much smaller quantities than iron or nickel. **Cobalt arsenide,** $CoAs_2$ (p. 783), as SMALTITE, forms cubic crystals isomorphous with pyrites and is the most important mineral containing cobalt, whilst COBALTITE is the corresponding cubic **cobalt sulpharsenide,** CoSAs. The principal source of cobalt is the rich silver vein near Cobalt in Ontario, which is the largest source of silver in the world, but contains also sulphides and arsenides of cobalt and nickel, and other minerals probably deposited from heated waters.

Metallurgy of Cobalt.

After roasting the ore and removing most of the iron, as described under nickel, cobalt is usually separated from other metals by wet methods, similar to those which are used in the laboratory, *e.g.*, copper and bismuth are precipitated as sulphides and the separation from

nickel is effected by precipitating the cobalt with sodium hypochlorite or bleaching powder, which does not throw down the nickel so readily as the cobalt.

The commercial metal is prepared by heating the oxide with charcoal. Pure cobalt is made either by igniting the oxalate, CoC_2O_4, or by electro-deposition.

Cobalt has no extensive commercial applications and is not isolated on any large scale. It has, however, been used in electro-plating as a substitute for nickel. Certain cobalt-alloys, including STELLITE (Co 55, W 25, Cr 15, Mo 5), have found an application in the manufacture of cutting tools, since they can be hardened without changing their dimensions, so that a tool, *e.g.*, for cutting screw-threads, can be cut to its finished dimensions prior to hardening and without making any allowance for distortion, expansion, or shrinkage; stellite has the further advantage of being very resistant to the action of nitric acid. Cobalt has also been used instead of tungsten in making steel for permanent magnets.

Properties of Cobalt.

(*a*) *Physical Properties.*—Cobalt is a silver-white metal closely resembling iron. Its density, 8·8, is substantially the same as that of nickel; its melting-point, 1480°, is intermediate between those of iron and nickel. It is more magnetic than nickel and retains its magnetism up to 1115°. Like nickel, it can be deposited from solution by a process of electro-plating.

(*b*) *Alloys.*—Cobalt is isomorphous with nickel both in the magnetic and in the non-magnetic form (Fig. 265, p. 776); it also forms complete series of solid solutions with chromium and with γ-iron; but it will only take up 10 per cent. of copper in solid solution when in the non-magnetic form, and 8 per cent. when in the magnetic form. With other elements it forms the compounds CoSb, Co_2Sn, Co_2P, $CoZn_4$, and four **silicides,** Co_2Si, CoSi, $CoSi_2$, and $CoSi_3$.

(*c*) *Chemical Properties.*—When reduced from the oxide by hydrogen at a low temperature, cobalt is pyrophoric, igniting in contact with the air, like iron and nickel when prepared in a similar manner; this action may perhaps be attributed to the solubility of hydrogen in the metal (60 to 150 vols.) and its catalytic oxidation by air in presence of the metal. Like iron, the massive metal oxidises only slowly when heated, but burns at a high temperature to the oxide, Co_3O_4, compare Fe_3O_4.

Cobalt decomposes steam at a red heat. It dissolves slowly in dilute hydrochloric and sulphuric acids, and much more rapidly in nitric acid, but may also be brought into the passive state. When heated in ammonia it forms the **nitride,** Co_4N_2.

(*d*) *Cobalt Carbonyls.*—**Cobalt tetracarbonyl,** CoC_4O_4, is formed when the metal is heated in carbon monoxide under 100 atmospheres

pressure at 150° to 200°; it melts at 51° and when heated at 60° loses a quarter of its carbon monoxide and leaves the **tricarbonyl,** CoC_3O_3, or a polymer, in the form of black crystals which are decomposed completely when heated above 60°.

Oxides of Cobalt.

Cobaltous oxide, CoO, resembles ferrous oxide in being less stable than the higher oxides. It is formed as a light brown powder by reducing the higher oxides in hydrogen below 350° (compare FeO from Fe_2O_3), or in a current of carbon dioxide at a red heat. **Cobaltous hydroxide,** $Co(OH)_2$, is precipitated by adding potassium hydroxide to a solution of a cobaltous salt. It is rose-red in colour, but absorbs oxygen and becomes brown on exposure to air.

Cobaltic oxide or **cobalt sesquioxide,** Co_2O_3, is formed as a dark brown powder by igniting cobaltous nitrate, just as ferric oxide is obtained by igniting ferrous sulphate,

$$4Co(NO_3)_2 = 2Co_2O_3 + 8NO_2 + O_2.$$

Cobaltic hydroxide, $Co(OH)_3$, is said to be precipitated as a brownish-black powder by the action of a hypochlorite on a cobaltous salt, as in the commercial separation of cobalt from nickel,

$$2CoCl_2 + NaOCl + 4NaOH + H_2O = 2Co(OH)_3 + 5NaCl,$$

but the precipitate often contains more oxygen than this hydroxide and may contain a hydrated dioxide, CoO_2 aq. (compare nickel). It liberates chlorine from hydrochloric acid and oxygen when dissolved in oxy-acids, but forms a fairly stable acetate.

Cobalto-cobaltic oxide, Co_3O_4, corresponding with magnetite, Fe_3O_4, is formed by igniting any of the other oxides in the air. When crystallised it forms black octahedral crystals, with a metallic lustre, but these are not magnetic.

Cobalt dioxide, CoO_2, is probably an intermediate compound in the separation of oxygen by warming bleaching powder with a cobalt salt, but has not been clearly distinguished from cobaltic hydroxide. A series of stable salts has, however, been prepared by fusing the sesquioxide with bases in the electric furnace, *e.g.*, **magnesium cobaltite,** $MgCoO_3$, and two forms of **barium cobaltite,** $BaCoO_3$ and $BaCo_2O_5$.

Sulphides and Arsenides.

Cobalt monosulphide, CoS, is precipitated by adding an alkaline sulphide to a soluble cobaltous salt; it is not precipitated in acid solutions and dissolves slowly in cold dilute hydrochloric acid. Cobalt may also occur as an isomorphous constituent of pyrrhotite or magnetic pyrites, $[Fe,Co,Ni]_3S_4$.

Cobalt disulphide is not known as a mineral, but a corresponding **cobalt sulpharsenide,** $CoSAs$, and **cobalt arsenide,** $CoAs_2$, are each

known in a cubic form corresponding with pyrites and in an orthorhombic form corresponding with marcasite.

Cobaltous Salts.

Cobaltous chloride, $CoCl_2$, is formed in blue scales when metallic cobalt is burnt in chlorine gas. It gives a blue solution in alcohol, which becomes rose-coloured on dilution. Aqueous solutions deposit red crystals of the **hexahydrate** $CoCl_2,6H_2O$, up to 50°; above this temperature a **dihydrate,** $CoCl_2,2H_2O$, is deposited; a red and a blue form of each hydrate have been described. Complete drying gives the blue anhydrous chloride. The rose-coloured aqueous solutions become blue on adding strong hydrochloric or sulphuric acid or alcohol, and from the first of these solutions a blue compound, $CoCl_2,3HCl,H_2O$, has been crystallised out at a low temperature. Cobalt chloride has been used as a "sympathetic ink," since the almost invisible rose colour of the dilute solution becomes blue and can be clearly seen when the chloride is dehydrated by warming. The corresponding fluoride, bromide, and iodide have also been described.

Cobaltous sulphate, $CoSO_4,7H_2O$, prepared by dissolving the metal or its oxide or carbonate in dilute sulphuric acid, forms red crystals isomorphous with ferrous sulphate. Above 40°, the **hexahydrate,** $CoSO_4,6H_2O$, separates in crystals isomorphous with $ZnSO_4,6H_2O$; salts with $4H_2O$ and $1H_2O$ have also been described, as well as **double-sulphates** such as $K_2SO_4,CoSO_4,6H_2O$.

Cobaltous nitrate, $Co(NO_3)_2$, prepared by dissolving the metal or its oxide or carbonate in nitric acid, crystallises from water with $9H_2O$, $6H_2O$, or $3H_2O$, according to the temperature; the ordinary form is the **hexahydrate,** $Co(NO_3)_2,6H_2O$. When heated, it liberates oxides of nitrogen and leaves a residue of the sesquioxide.

Cobaltous carbonate, like nickel carbonate, although insoluble in water, has been prepared in an anhydrous form, $CoCO_3$, and as a **hexahydrate,** $CoCO_3,6H_2O$.

Cobaltous cyanide, $CoC_2N_2,3H_2O$, is precipitated (like nickel cyanide, NiC_2N_2) by the addition of potassium cyanide to a solution of a cobaltous salt. It dissolves in an excess of potassium cyanide, but unlike nickel forms an unstable **potassium cobaltocyanide,** $K_4CoC_6N_6$, which oxidises very readily to the cobalticyanide, $K_3CoC_6N_6$ (p. 800).

Cobaltic Salts.

The tervalent cobaltic salts are much less stable than the ferric salts and can as a rule be prepared only by special methods. Thus **cobaltic fluoride,** CoF_3, is formed as a green powder by electrolytic oxidation of cobaltous fluoride in a platinum dish; it is hydrolysed by water to cobaltic hydroxide (compare the plumbic salts, p. 697).

Cobaltic sulphate, $Co_2(SO_4)_3,18H_2O$, compare $Al_2(SO_4)_3,18H_2O$, is

prepared by electrolytic oxidation of cobaltous sulphate in a divided cell (compare the preparation of persulphates, p. 349); it crystallises in blue, silky needles and forms a series of **cobaltic alums,** *e.g.*, $NH_4Co(SO_4)_2,12H_2O$, crystallising in blue octahedra.

Cobaltic salts are, however, much more stable in presence of ammonia, and a number of cobaltic compounds of these and of analogous types are described below.

Co-ordinated Compounds.

Hydrates and Ammines.

Attention has already been directed (p. 739) to the fact that chromic chloride forms two AMMINES, with five and with six molecules of ammonia respectively,

$$CrCl_3,5NH_3 \qquad CrCl_3,6NH_3.$$

These have the remarkable property that, whilst the whole of the chlorine in the latter compound can be precipitated by silver nitrate, only two-thirds of the chlorine in the former compound can be precipitated. These results are explained, on lines first suggested by Werner, by assuming that in the hexammine, $CrCl_3,6NH_3$, the six molecules of ammonia are associated directly with the metallic ion or radical, and that in pentammine, $CrCl_3,5NH_3$, one of the chlorine atoms is locked up in a similar manner, thus:

$$[Cr'''.6NH_3]Cl_3 \qquad [Cr'''.5NH_3\,Cl]Cl_2.$$

These compounds, which do not depend on the main valencies of the atoms, but on the "residual affinity" of the unsaturated molecules of water or of ammonia, etc., are described as CO-ORDINATION COMPOUNDS. They are particularly abundant amongst elements of small atomic volume where the groups can cluster most closely around the metallic nucleus, as in the elements of the transition groups which occupy the troughs of the atomic volume curve.

An analogous conception may be used to account for the stability of the ferrocyanides and ferricyanides, in which six cyanogen groups are associated with an atom of iron, *e.g.*,

$$K_4[Fe''.6CN] \text{ and } K_3[Fe'''.6CN].$$

In each of these cases the normal chemical properties of the heavy metal are wholly or partly disguised by conversion into a COMPLEX ION, which differs widely in its properties from the simple ions of the metal.

These phenomena are specially well developed in the tervalent cobaltic salts, which form extremely stable compounds and are very readily prepared in this form.

Cobaltammine Chlorides.

Compound.	*Formula.*	*Colour.*	*Solubility.*
Purpureo-cobaltic chloride	$CoCl_3,5NH_3$ or $[Co.5NH_3.Cl]Cl_2$	Red	1/250
Roseo-cobaltic chloride	$CoCl_3,5NH_3,H_2O$ or $[Co.5NH_3.H_2O]Cl_3$	Pink	1/5
Luteo-cobaltic chloride	$CoCl_3,6NH_3$ or $[Co.6NH_3]Cl_3$.	Yellow	1/17

(*a*) **Purpureo-cobaltic chloride,** $CoCl_3,5NH_3$, or $[Co.5NH_3.Cl]Cl_2$, is a PENTAMMINE, which can be prepared as a reddish-violet (almost black) crystalline powder by oxidising an ammoniacal solution of cobaltous chloride, $CoCl_2$, *e.g.*, with hydrogen peroxide. Only two-thirds of its chlorine can be precipitated by silver nitrate in the cold, and cold strong sulphuric acid displaces only two-thirds of the chlorine as hydrochloric acid, giving a chlorosulphate, $CoCl(SO_4),5NH_3$, or $[Co.5NH_3.Cl]SO_4$, from which the chlorine cannot be displaced by cold silver nitrate; even more remarkable perhaps is the fact that the ammonia is not removed by the sulphuric acid. The whole of the chlorine can, however, be removed by the action of moist silver oxide, giving a basic compound, $Co(OH)_3,5NH_3,H_2O$ or $[Co.5NH_3.H_2O](OH)_3$, containing an additional molecule of water.

(*b*) **Roseo-cobaltic chloride,** $CoCl_3,5NH_3,H_2O$, or $[Co.5NH_3.H_2O]Cl_3$, is formed by neutralising this base with hydrochloric acid, or by digesting the purpureo-chloride itself with warm dilute ammonia. It is a red powder which has the same composition as the purpureo-chloride except for the addition of a molecule of water, but differs from it in being freely soluble in cold water; moreover, the whole of the chlorine can be precipitated by silver nitrate in the cold. The reconversion of the roseo-salt into the purpureo-salt can be effected by drying at 100° and also takes place slowly in solution.

(*c*) **Luteo-cobaltic chloride,** $CoCl_3,6NH_3$, or $[Co.6NH_3]Cl_3$, is a HEXAMMINE, which differs from the purpureo-chloride in containing six instead of five molecules of ammonia, and three instead of two atoms of chlorine which can be precipitated by silver nitrate. It was prepared (but not isolated) more than a century ago by atmospheric oxidation of an ammoniacal solution of cobaltous chloride. It can be prepared by heating either the roseo-salt or the purpureo-salt with strong ammonia in a closed vessel, and forms orange-coloured crystals. It is stable up to 130° when anhydrous and is not readily decomposed by boiling water. It is also not decomposed by hydrochloric acid even under pressure; but alkalies decompose it completely, and alkaline sulphides give an immediate precipitate of cobaltous sulphide, CoS.

The luteo-chloride is typical of a long series of COBALT HEXAMMINE SALTS, in which the tervalent radical, $[Co(NH_3)_6]'''$, behaves like a tervalent alkali metal, *e.g.*, the hydroxide, $[Co.6NH_3](OH)_3$ (known only in solution), is a

strong alkali and absorbs carbon dioxide from the air; and the fluoride forms acid salts, $[Co.6NH_3]F_3,3HF$, compare KHF. Roseo-cobaltic chloride is also one of a series of tervalent COBALT AQUO-PENTAMMINE SALTS, in which the radical, $[Co.5NH_3.H_2O]'''$, is combined with acid radicals. Purpureo-cobaltic chloride is the type of a series of COBALT ACIDO-PENTAMMINE SALTS, in which the bivalent radical, $[Co.5NH_3.X]''$, may contain X = Cl, Br, I, NO_3, in addition to showing variations in the acid-radical with which the complex basic radical is associated.

Cobaltinitrites.

(*a*) *Potassium Cobaltinitrite.*—When a solution of a cobaltous salt, acidified with acetic acid, is acted on by potassium nitrite, oxidation of the cobalt occurs and a double nitrite is formed,

$$CoCl_2 + 5KNO_2 + 2HNO_2 = K_3Co(NO_2)_6 + 2KCl + NO + H_2O.$$

This salt can be regarded as a co-ordination compound in which the six nitro-groups play the part of the six molecules of ammonia in the hexammine, whilst the three atoms of potassium represent the three atoms of chlorine,

$$[Co'''.6NO_2]K_3\ ;\quad \text{compare}\quad [Co'''\ 6NH_3]Cl_3.$$

Potassium cobaltinitrite, $K_3Co(NO_2)_6$, is a stable yellow salt which is only sparingly soluble in water. It is used as a pigment under the name of COBALT YELLOW. Ammonium sulphide immediately precipitates cobalt sulphide, and warm alkalies precipitate the brown hydroxide; but it is very resistant to acids, which only attack it when hot, and is therefore entirely different from other metallic nitrites, the properties of the nitrite radical being masked almost as completely as those of the ammonia in the ammines. It is the type of a series of COBALTINITRITES, $R_3Co(NO_2)_6$, which undergo double decomposition (like the ferrocyanides, ferricyanides, etc.) without breaking up the complex acid radical, *e.g.*, **sodium cobaltinitrite,** $Na_3Co(NO_2)_6$, is much more soluble than the potassium salt and can be used as a test for potassium in qualitative analysis.

(*b*) *Croceo- and Flavo-cobaltic Salts.*—When a solution of cobalt chloride and sodium nitrite, instead of being oxidised by nitrous acid, is oxidised by a current of air in presence of ammonium chloride, it gives an orange-coloured **croceo-cobaltic chloride,** $CoCl(NO_2)_2,4NH_3$ or $[Co.4NH_3.2NO_2]Cl$; this is a TETRAMMINE in which four molecules of ammonia are co-ordinated with the cobalt in addition to two nitrite radicals. **Croceo-cobaltic nitrate,** $[Co.4NH_3.2NO_2]NO_3$, and a large number of other univalent salts of the same series are also known, This series of salts is of special interest because of the existence of a well-marked isomerism between the "croceo" and the "flavo" salts, which must be represented by identically the same formulæ, but appear to differ in the way in which the six radicals are grouped around the cobalt atom.

Flavo-cobaltic nitrate, $[Co.4NH_3.2NO_2]NO_3$, is prepared by adding nitric acid, sodium nitrite, and then an excess of nitric acid to a **carbonate-tetrammine,** $[Co.4NH_3.CO_3]NO_3$, prepared by oxidising cobalt chloride in presence of ammonium carbonate and ammonium nitrate. This compound contains a disguised carbonate group, which will not precipitate chalk from calcium chloride ; but treatment with nitric and nitrous acids as described above has the effect of displacing the bivalent carbonate group CO_3 by two univalent nitro-groups NO_2, giving a yellow flavo-salt which is ten times more soluble (1/33 instead of 1/340) than the isomeric croceo-salt. It differs from the croceo-salt also in that the two NO_2 groups, which were introduced together in place of a CO_3 group, are displaced together from the flavo-salt by boiling it with strong hydrochloric acid ; the product is a green univalent **cobalt tetrammine chloride,** $CoCl_3,4NH_3$ or $[Co.4NH_3.Cl_2]Cl$, in which only one-third of the chlorine can be precipitated. When treated in the same way, only one of the NO_2 groups of the croceo-salt is displaced, giving a deep red salt, $CoCl_2NO_2,4NH_3$ or $[Co.4NH_3.NO_2.Cl]Cl$, in which one-half of the chlorine can be precipitated by silver nitrate.

(*c*) *Non-ionisable Cobaltic Compounds.*—By spontaneous oxidation of cobalt chloride in presence of certain proportions of ammonium chloride, sodium nitrite, and ammonia, it is possible to prepare a TRIAMMINE of the formula

$$Co(NO_2)_3,3NH_3 \quad \text{or} \quad [Co.3NH_3.3NO_2].$$

This is intermediate between the hexammine, $[Co.6NH_3]Cl_3$, which contains a complex tervalent *basic* radical, and the cobaltinitrite, $[Co.6NO_2]K_3$, which contains a complex tervalent *acid* radical. It contains equal numbers of molecules of ammonia and of nitro-groups, and is a neutral compound, which does not dissociate when dissolved in water, and does not show the ordinary reactions of any of its constituent radicals. The green chromic sulphate described above (p. 740) is a compound of similar type and may be formulated as

$$Cr_2(SO_4)_3,6H_2O \quad \text{or} \quad [Cr.\tfrac{3}{2}SO_4.3H_2O]_2.$$

Cobalticyanides.

(*a*) *Potassium Cobalticyanide.*—In the case of iron, the ferricyanide, $K_3FeC_6N_6$, is much less stable than the ferrocyanide, $K_4FeC_6N_6$, and changes back into the latter compound so readily as to be an effective oxidising agent. In the case of cobalt, this condition is reversed, since when cobaltous chloride is precipitated and redissolved in an excess of potassium cyanide the **potassium cobaltocyanide,** $K_4CoC_6N_6$, which is first formed (and which can be precipitated by alcohol as an amethyst-coloured powder) changes very readily into **potassium cobalticyanide,** $K_3CoC_6N_6$, and is a very powerful reducing agent. Thus, on the addition of an acid it actually liberates hydrogen, as shown in the equation

$$2K_4CoC_6N_6 + 2HCl = 2K_3CoC_6N_6 + 2KCl + H_2 ;$$

when the oxidation takes place rapidly in presence of air, however, the action is modified in such a way that hydrogen peroxide is formed instead of hydrogen, as shown in the equation

$$2K_4CoC_6N_6 + 2HCl + O_2 = 2K_3CoC_6N_6 + 2KCl + H_2O_2.$$

Potassium cobalticyanide is a very stable compound and separates from water in yellow crystals isomorphous with potassium ferricyanide.

(*b*) *Cobalticyanic Acid and the Cobalticyanides.*—Potassium cobalticyanide, like the ferricyanide, can be used to prepare, by double decomposition, a series of COBALTICYANIDES. **Copper cobalticyanide,** $Cu_3(CoC_6N_6)_2$, forms a blue precipitate, and **silver cobalticyanide,** $Ag_3CoC_6N_6$, a white precipitate. By the action of hydrogen sulphide on copper cobalticyanide, **cobalticyanic acid,** $H_3CoC_6N_6$, is formed and can be crystallised out in silky needles; it is a stable compound, and is not attacked even by strong nitric acid.

Cobalt Pigments.

Cobalt, like chromium, forms an important series of pigments, which have the advantage of being extremely stable.

(*a*) SMALT is a potash glass coloured blue with cobalt. It has long been prepared by fusing a cautiously-roasted cobalt ore with sand and potash. The less oxidisable metals are left as arsenides after roasting, and remain undissolved in the glass, from which they separate as a fusible quasi-metallic "spiess" (p. 528) at the bottom of the crucible. The glass is ladled out, quenched in water, ground, and graded by sedimentation in water. The product is a permanent blue pigment which resists the action of acids, and can also be used in enamel work.

(*b*) COBALT BLUE, or "Thenard's blue," probably contains a **cobalt aluminate,** $CoAl_2O_4$. It can be prepared by precipitating a mixture of cobalt nitrate and alum with sodium carbonate, and igniting the mixed hydroxides; the cobalt may also be precipitated separately as hydroxide, phosphate, or arsenate and ignited with precipitated alumina. The product is ground with water and dried.

(*c*) CŒRULEUM, which has a greener tinge than cobalt blue, is prepared by precipitation from a mixture of cobalt nitrate and sodium stannate followed by ignition. It probably contains a **cobalt stannate,** *e.g.*, $CoSnO_3$. The colour can also be modified by the introduction of chromic salts.

(*d*) COBALT GREEN, or "Rinmann's green," is a **cobalt zincate,** prepared in a similar manner to cobalt blue but using zinc oxide in place of alumina.

(*e*) COBALT YELLOW is **potassium cobaltinitrite,** $K_3Co(NO_2)_6$. It is a yellow pigment, which blackens less readily than chrome yellow, $PbCrO_4$, when exposed to the action of hydrogen sulphide. When used on porcelain, it burns to a very pure blue.

Detection and Estimation.

The methods used to separate cobalt and nickel, and to detect and estimate these two metals, are described below under nickel (p. 809).

28. NICKEL. Ni = 58·68.

Occurrence of Nickel.

Nickel is very widely distributed in igneous rocks to the extent of about 0·02 per cent. It is also found in meteorites, which sometimes contain more nickel than iron. Segregations of nickel ore are of two types:

(*a*) *Sulphide Ores.*—Nickel appears in combination with sulphur, arsenic, and antimony in compounds analogous to those of iron, *e.g.*,

(i) As MILLERITE, NiS, as KUPFER-NICKEL, NiAs, and as NiSb, in hexagonal crystals which are isomorphous with ZnS as wurtzite, and with CdS as greenockite, but not with the cubic sulphides such as troilite, FeS, blende, ZnS, galena, PbS, or argentite, Ag_2S.

(ii) As Ni_3S_4 (?), isomorphous with Fe_3S_4 (?), in nickeliferous pyrrhotite or magnetic pyrites.

(iii) As $NiAs_2$ and NiSAs, two compounds which are isodimorphous with FeS_2, occurring both in the cubic system (compare pyrites) and in the orthorhombic system (compare marcasite).

The principal source of nickel is an igneous dyke at Sudbury in Ontario in which pyrrhotite containing nickel has separated from a siliceous magma. Similar sulphide deposits containing nickel are found in many other countries.

(*b*) *Silicate Ores.*—A secondary source of nickel is GARNIERITE, $Ni_2H_4Si_3O_{10}$, a serpentine formed by the decomposition of sub-silicic rocks containing nickel. The orthosilicate, Ni_2SiO_4, appears to have been converted into a hydrated silicate by elimination of two-thirds of the bivalent metal (but probably of magnesium rather than nickel where both are present), perhaps according to the equation

$$3Ni_2SiO_4 + 2H_2O + 4CO_2 = Ni_2H_4Si_3O_{10} + 4NiCO_3;$$

just as olivine, Mg_2SiO_4, is converted into serpentine by eliminating one-fourth of the bivalent metal (p. 511),

$$\underset{\text{Olivine}}{2Mg_2SiO_4} + 2H_2O + CO_2 = \underset{\text{Serpentine}}{Mg_3H_4Si_2O_9} + MgCO_3.$$

Metallurgy of Nickel.

The metallurgy of nickel (like that of copper, p. 828) is complicated by the presence of large quantities of iron, since the ore usually contains only from 3 to 10 per cent. of nickel. The manufacture of

nickel therefore includes a separation from iron in two stages and a separation from copper, in addition to the final reduction to metal.

(*a*) *Preliminary Separation of Iron.*—The sulphide ore is roasted in large heaps and then melted in small blast-furnaces. In the roasting, ferrous sulphide is oxidised in preference to nickel or copper, and the ferrous oxide thus produced is converted in the furnaces into a slag of ferrous silicate,

$$2FeS + 3O_2 = 2FeO + 2SO_2$$
$$2FeO + SiO_2 = Fe_2SiO_4.$$

The sulphides of nickel and copper are separated as a CRUDE MATTE (p. 528) of melted sulphides, which still contains more iron than nickel.

(*b*) *Removal of Iron.*—The remainder of the iron is best removed by oxidising the crude matte in a Bessemer converter, with a silicate lining, sand being added to form a siliceous slag. This slag consists mainly of ferrous silicate, but contains also 2 to 10 per cent. of nickel, and is therefore worked up again with a further batch of ore. The REFINED MATTE consists of sulphides of nickel and copper with only about 0·5 per cent. of iron.

(*c*) *Separation of Copper.*—Copper in the refined matte is separated from the nickel by melting with sodium sulphate and coal, when the sulphides of copper and iron pass into the upper layer or slag of sodium sulphide, whilst the nickel sulphide remains in the lower layer.

(*d*) *Reduction.*—The nickel sulphide is powdered and roasted until quite free from sulphur; the oxide is then reduced by heating with carbon, usually at a temperature insufficient to melt the nickel.

Silicate ores are converted into sulphides by smelting with calcium sulphide (or a mixture of calcium sulphate and coal), giving a slag of calcium silicate and a matte of nickel sulphide, which is worked up as before.

The MOND PROCESS of separating nickel from the matte is described below (p. 806).

Properties of Nickel.

(*a*) *Physical Properties.*—Metallic nickel resembles iron very closely. Thus, it melts at 1452°, a little below the melting-point of iron (1530°), and is also rather more volatile than iron in the electric furnace. Its density, 8·8, is greater than that of iron (7·8), and its tensile strength is also higher. It is magnetic at low temperatures, but becomes non-magnetic at 320°. The metal has a steel-grey colour and takes a high polish; like copper and silver, it can be used in "electro-plating," *i.e.*, a thin layer of metal can be deposited by the electric current from a solution of nickel ammonium sulphate in a coherent form on a cathode of a baser metal and used to protect it from oxidation or corrosion.

(*b*) *Chemical Properties.*—Nickel shows much more resistance to oxidation than iron; nickel wire will, however, burn in oxygen, and the freshly-reduced metal may ignite spontaneously in the air, perhaps on account of the occluded hydrogen which it contains. It does not rust, and decomposes steam only slowly. It dissolves only

slowly in dilute acids, except nitric acid and aqua regia, and like iron becomes passive in strong nitric acid. Its resistance to oxidation and to attack by acids and alkalies has led to the extensive use of nickel crucibles, spatulas, tongs, etc., in the laboratory, whilst nickel-plating (usually over copper) is used extensively for protecting iron from rust and securing a brilliant polished surface, *e.g.*, on the bright parts of bicycles, etc.

(*c*) *Hydrogenation by Means of Nickel.*—Nickel absorbs 17 times its volume of hydrogen and is of very great value as a catalyst in promoting combination with (or removal of) hydrogen, especially in organic compounds. Thus, it is used for removing carbon disulphide from coal-gas, by converting it into hydrogen sulphide and methane,

$$CS_2 + 4H_2 = CH_4 + 2H_2S,$$

for eliminating carbon monoxide from hydrogen, by conversion into methane,

$$CO + 3H_2 = CH_4 + H_2O,$$

and for converting carbon monoxide and steam into carbon dioxide and hydrogen,

$$CO + H_2O = CO_2 + H_2.$$

It can also be used to convert ethylene into ethane,

$$C_2H_4 + H_2 = C_2H_6,$$

or benzene into hexahydrobenzene,

$$C_6H_6 + 3H_2 = C_6H_{12}.$$

Its most important application, however, is for promoting the hardening of oils and fats by combination with hydrogen.

Alloys of Nickel.

(*a*) *Chromium.*—Chromium and nickel give an eutectic alloy ($Cr = 57{\cdot}5$ per cent., $Ni = 42{\cdot}5$ per cent., m.-p. 1280°), but both

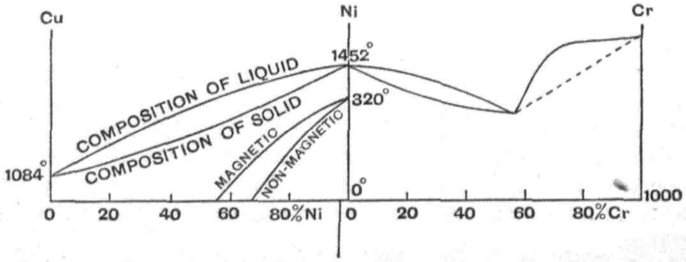


FIG. 273.—EQUILIBRIUM-DIAGRAMS FOR COPPER, NICKEL, AND CHROMIUM.
The magnetic change-point at 320° has been displaced on the scale of temperatures to 1320° in order to compress the diagram.

metals separate from the melt as isomorphous mixtures (Fig. 273). On account of its high electrical resistance and its great resistance to

oxidation (compare "stainless steel"), an alloy of nickel and chromium is used in preference to pure nickel as NICHROME WIRE for winding electric furnaces.

(*b*) *Iron.*—The non-magnetic high temperature form of nickel is isomorphous with γ-iron, but the magnetic form gives a compound, $FeNi_2$, instead of a solid solution (Fig. 265). Reference has already been made (p. 776) to the use of nickel steel for armour-plating, and for non-expanding alloys; a nickel steel containing about 46 per cent. of nickel has nearly the same coefficient of expansion as glass and is used as a substitute for platinum under the name of PLATINITE for sealing into glass.

(*c*) *Cobalt.*—Nickel is isodimorphous with cobalt and forms complete series of solid solutions with the metal, both in the magnetic and in the non-magnetic form (Fig. 265, p. 776).

(*d*) *Copper.*—Nickel also forms two series of solid solutions with copper, one magnetic and the other non-magnetic, but these correspond with a magnetisation of copper only at temperatures very much below 0° (Fig. 273). Solid solutions of nickel and copper melt at a higher temperature than copper (Fig. 273); they are harder and have a much lower electrical conductivity than either metal (Fig. 274). Alloys of nickel and copper are therefore used extensively in making electrical resistances; thus, CONSTANTAN, Ni 40 per cent., Cu 60 per cent., which has a very small temperature coefficient as well as a high resistance, is used for winding resistance boxes; it is also used in conjunction with copper for making sensitive thermal junctions for pyrometers at moderate temperatures; MANGANIN, an alloy of very similar properties, contains Cu 84 per cent., Mn 12 per cent., Ni 4 per cent., manganese being also isomorphous with copper. Nickel is also used to increase the hardness of copper boiler tubes, etc., whilst alloys of nickel containing both copper and zinc (*i.e.*, brass hardened by nickel), *e.g.*, Cu 50, Ni 30, Zn 20, or Cu 57, Ni 7, Zn 36 per cent., are used as white metal or GERMAN SILVER for electro-plated goods. Nickel coins usually contain 75 per cent. of copper and 25 per cent. of nickel, but pure nickel can also be used for this purpose.

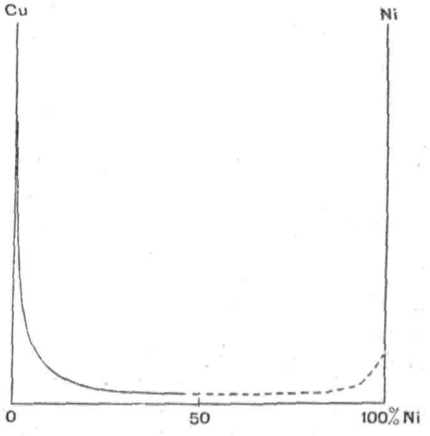


FIG. 274.—ELECTRICAL CONDUCTIVITY OF SOLID SOLUTIONS OF COPPER AND NICKEL.

Nickel Carbonyl, NiC_4O_4.

Nickel combines with carbon monoxide at temperatures below 100° to form **nickel carbonyl,** NiC_4O_4. This is a liquid boiling at 43° and freezing at $-25°$; the vapour, which is very poisonous, has a density corresponding with the formula NiC_4O_4. It is noteworthy that nickel, which requires eight electrons to complete its outer shell (p. 550), unites with four bivalent CO radicals to form a tetracarbonyl, NiC_4O_4; iron, which requires ten electrons, unites with 5CO to form a volatile pentacarbonyl, FeC_5O_5; whilst molybdenum, which requires twelve electrons, forms a hexacarbonyl, MoC_6O_6.

Nickel carbonyl is decomposed at 180° to 200°, depositing nickel and liberating carbon monoxide. The formation and decomposition of nickel carbonyl are used in the MOND NICKEL PROCESS for separating pure nickel from its ores, as follows:

(*a*) *Roasting.*—The refined (or Bessemerised) matte, consisting of copper and nickel sulphides with some ferrous sulphide, is roasted to remove the whole of the sulphur, ground, and sieved. The roasted matte is then enriched by extracting it with dilute sulphuric acid, which dissolves the copper oxide in preference to the nickel oxide, whereby the nickel content is raised from 35 to 51 per cent., whilst the copper is diminished from 42 to 21 per cent. and the iron from 5 to 3 per cent.

(*b*) *Reduction.*—The enriched oxide is "reduced" by means of water-gas at a temperature of 300°, when the nickel and copper are separated in an active form, whilst the ferric oxide resists reduction. At this temperature there is also a preferential oxidation of the hydrogen of the water-gas, giving a residual gas rich in carbon monoxide, which can be used for making the carbonyl after passing it through a retort containing hot charcoal to convert any carbon dioxide to carbon monoxide.

(*c*) *Volatilisation.*—The mixture of nickel and copper with ferric oxide is "volatilised" at a temperature of 50° to 100° in a current of gas (taken from the reducer and enriched) containing 80 per cent. of carbon monoxide.

(*d*) *Decomposition.*—The product, containing 2 per cent. of NiC_4O_4, is "decomposed" at 180° in a tower filled with pellets of pure nickel, which take up the nickel from the carbonyl and are withdrawn as they increase gradually in size to about ¼-inch.

(*e*) *Circulation of Gas and Ore.*—The gas from the decomposer is returned to the volatiliser, and the metal (reduced oxide) from the volatiliser is passed back to the reducer to be rendered active again (perhaps by saturation with hydrogen) by contact with the reducing gases. When about 60 per cent. of the nickel has been volatilised, the residual metal is returned to the roaster to be oxidised, and the accumulation of copper is removed in the normal way by extracting the oxide with sulphuric acid.

Oxides of Nickel.

Nickel monoxide, NiO, is found as a mineral in green octahedra, and can be prepared, by heating the hydroxide, the carbonate, or the nitrate, as a green powder which becomes yellow when heated. The **hydroxide,** $Ni(OH)_2$, is prepared as an apple-green precipitate, by

adding an alkaline hydroxide to a soluble nickel salt, and dissolves to a blue solution in ammonia (compare copper).

Nickel sesquioxide, Ni_2O_3, can be prepared as a black powder by gently roasting the carbonate or nitrate; by heating more strongly it is decomposed again to the monoxide. The black precipitate formed by the action of an alkaline hypochlorite on a nickel salt may be either the **trihydroxide,** $Ni(OH)_3$, or a hydrated form of the **dioxide,** NiO_2, the **barium salt** of which, $BaNi_2O_5$, has been prepared by heating the sesquioxide with barium carbonate in an electric furnace.

Sulphides and Arsenides.

The sulphides of nickel correspond closely with the isomorphous sulphides of iron, and are commonly associated with them. The most important of these compounds, **nickel monosulphide,** NiS, is soluble in presence of acids (which dissolve it only slowly, p. 809), but is precipitated from solutions of nickel salts by alkaline sulphides.

The arsenides of nickel are remarkable for their isomorphism with the sulphides, *e.g.*, NiSAs and $NiAs_2$ are both isodimorphous with FeS_2.

Salts of Nickel.

Nickel resembles zinc (p. 868) in giving only one stable series of salts, in which metal is bivalent. In this respect it differs from cobalt, which forms in addition a series of tervalent cobaltic salts, and still more from iron, of which the tervalent ferric salts are more stable than the bivalent ferrous salts. The bivalent salts of nickel resemble those of copper, the metal which follows it in the periodic classification of the elements; but nickel differs also from copper in that there are no salts to correspond with the univalent cuprous salts (p. 838). A noteworthy feature of the bivalent salts of nickel is their readiness to combine with $6H_2O$, with $6NH_3$, or with $3H_2O + 3NH_3$, etc., perhaps because they form co-ordinated compounds of a less stable character than those of cobalt.

Nickel chloride, $NiCl_2$, is formed in golden scales by the action of chlorine on nickel. It can also be prepared by evaporating to dryness a solution of the oxide or carbonate in strong hydrochloric acid. The anhydrous chloride can be sublimed in the absence of air, but when heated in air it liberates chlorine and leaves a residue of oxide,

$$2NiCl_2 + O_2 = 2NiO + 2Cl_2.$$

The chloride crystallises from water in green crystals of the **hexahydrate** $NiCl_2,6H_2O$, and absorbs ammonia, forming an almost colourless **hexammine,** $NiCl_2,6NH_3$. The **fluoride, bromide,** and **iodide** are also known, both in anhydrous and hydrated forms.

Nickel cyanide, NiC_2N_2, differs from the chloride in being in soluble in water (it forms an apple-green precipitate), but dissolves

in an excess of potassium cyanide, forming a double salt, $NiC_2N_2,2KCN$; this double salt is, however, decomposed at once by dilute acids, and no stable compounds of the type of the ferrocyanides or ferricyanides are known. In this respect, therefore, nickel differs widely from iron and cobalt and shows a closer resemblance to copper and especially to zinc, which forms an insoluble cyanide, ZnC_2N_2, and a soluble double cyanide, $K_2ZnC_4N_4$, compare $K_2NiC_4N_4$.

Nickel sulphate, $NiSO_4$, prepared by dissolving the metal or its oxide or carbonate in dilute sulphuric acid, crystallises from water with $7H_2O$. A **hexahydrate,** $NiSO_4,6H_2O$, separates, however, in blue tetragonal crystals from 31° to 53°, and from 53° to 120° in green monosymmetric crystals; these two forms of the hexahydrate, if not merely polymorphic, are probably isomeric with one another (Fig. 275). When dried at 100° it gives the **monohydrate,** $NiSO_4,H_2O$, and at 280° a yellow **anhydrous sulphate** is formed. This unites with ammonia to form a violet **hexammine,** $NiSO_4,6NH_3$, whilst from concentrated solutions of the sulphate in aqueous ammonia dark blue tetragonal crystals separate, of the composition

$NiSO_4,4NH_3,2H_2O$ or
$NiSO_4,3NH_3,3H_2O$.

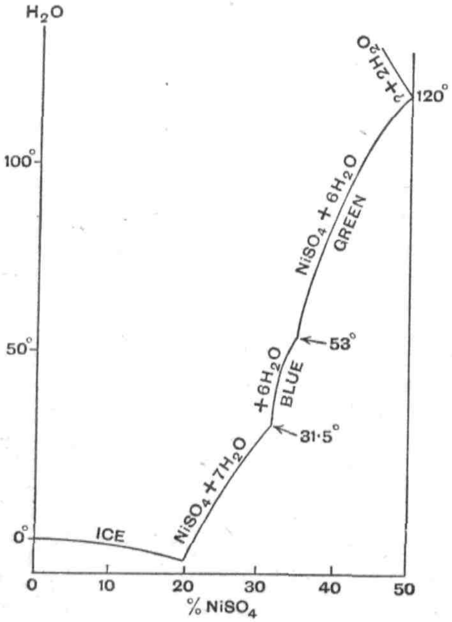


FIG. 275.—HYDRATES OF NICKEL SULPHATE.

Like other bivalent sulphates, nickel sulphate forms a series of double salts with the sulphates or the alkali metals, *e.g.*, **nickel ammonium sulphate,** $(NH_4)_2Ni(SO_4)_2,6H_2O$, compare $K_2Mg(SO_4)_2,6H_2O$, is used in electro-plating with nickel.

Nickel nitrate, $Ni(NO_3)_2,6H_2O$, crystallises in green tablets, dissolves in twice its weight of cold water, and deliquesces in moist air.

Nickel carbonate is usually precipitated only as a basic salt, but the compounds $NiCO_3$ and $NiCO_3,6H_2O$ have both been prepared in a crystalline form, the latter separating from a solution (prepared by the action of sodium bicarbonate and carbon dioxide on nickel nitrate) which probably contains nickel bicarbonate.

Detection and Estimation of Nickel and Cobalt.

(*a*) *Detection.*—Nickel and cobalt both yield an infusible magnetic powder like iron when reduced on charcoal in the flame of a blow-pipe ; when this powder is dissolved in nitric acid and the solution is evaporated to dryness, nickel gives a green stain, which becomes yellow on further heating, whilst cobalt dissolved in hydrochloric acid gives a rose-red solution which becomes blue on evaporation.

Nickel imparts a brownish-yellow colour to a borax bead in an oxidising flame and gives an opaque grey bead containing metallic nickel when heated in a reducing flame ; cobalt gives a beautiful blue colour to the borax bead.

In qualitative analysis nickel and cobalt are precipitated by ammonium sulphide as NiS and CoS ; they can be separated from MnS and ZnS by extracting with cold dilute hydrochloric acid in which the black sulphides of nickel and cobalt are almost insoluble.

(*b*) *Separation.*—The separation of nickel and cobalt is effected by various methods, but three of them depend on the greater readiness of cobalt to form tervalent compounds analogous to the ferric compounds.

(i) *Oxidation to Sesquioxide.*—Bromine water precipitates Co_2O_3, aq. from a neutral solution of cobalt, whilst nickel remains in solution.

(ii) *Separation of Cyanides.*—The precipitated sulphides are dissolved in concentrated hydrochloric acid in presence of potassium chlorate ; after evaporating off most of the hydrochloric acid and diluting again with water, the cyanides are precipitated and redissolved by the addition of potassium cyanide. By boiling the solution with a drop of acetic acid, the cobalt is converted into potassium cobalticyanide and cannot then be precipitated by sodium hypochlorite, whilst nickel remains as a simple double cyanide and is at once precipitated. Nickel can then be detected in the precipitate and cobalt in the filtrate by the ordinary dry methods of analysis, although the cobalticyanide does not give the reactions of a cobalt salt in solution.

(iii) *Separation of Nitrites.*—Cobalt can also be recognised and separated from nickel by precipitation as potassium cobaltinitrite, $K_3Co(NO_2)_6$.

(iv) *Organic Derivatives.*—Nickel can be detected by giving a scarlet precipitate, $Ni(C_4H_7O_2N_2)_2$, with dimethylglyoxime, $HON{:}C(CH_3){\cdot}C(CH_3){:}NOH$, in presence of ammonium or sodium acetate, and a yellow precipitate, $Ni(C_2H_5ON_4)_2,2H_2O$, with dicyanodiamide, $C_2H_4N_4$, in an alkaline solution. Cobalt (but not nickel) forms an insoluble orange-coloured compound with the sodium salt of nitroso-β-naphthol, $C_{10}H_6(NO){\cdot}OH$.

(*c*) *Estimation.*—Nickel is usually weighed as the **monoxide,** NiO, and cobalt as **cobalto-cobaltic oxide,** Co_3O_4. Thus,

(i) After converting nickel and cobalt into the double-cyanides as described above, the nickel that is precipitated by the alkaline hypochlorite may be ignited and weighed as the monoxide; the cobalt can then be precipitated as **mercurous cobalticyanide,** $Hg_3CoC_6N_6$, by mercurous nitrate in an acid solution, ignited, and weighed as Co_3O_4.

(ii) Cobalt may be weighed directly as **potassium cobaltinitrite,** $K_3Co(NO_2)_6$, after drying at 100°; the nickel remaining in solution can then be precipitated by caustic potash, ignited, and weighed as **nickel monoxide,** NiO.

(iii) Nickel can be weighed in combination with dimethylglyoxime, as described above, after drying at 120°; this compound also affords a sensitive colorimetric method for estimating traces of nickel. Cobalt can be estimated as metal by igniting and reducing in hydrogen the insoluble compound which it forms with nitroso-β-naphthol.

(iv) Nickel and cobalt are commonly estimated as **metal** by electro-deposition; if necessary the nickel in the mixed deposit is estimated with the help of dimethylglyoxime, and the proportion of cobalt calculated "by difference."

(*d*) *Atomic Weights.*—The atomic weight of nickel has been determined by converting nickel bromide, $NiBr_2$, into nickel by reduction in hydrogen and into silver bromide by precipitation with a known quantity of silver, thus giving the ratios Ni : $NiBr_2$ and $NiBr_2$: 2AgBr : 2Ag.

The atomic weight of cobalt has been determined by a similar analysis of cobalt bromide, Co : $CoBr_2$: 2AgBr : 2Ag, and also by determining the ratios $CoCl_2$: 2AgCl : 2Ag.

CHAPTER XLII

PALLADIUM AND PLATINUM GROUPS

	Atomic Number.	*Element.*	*Symbol.*		*Atomic Weight.*
{	44	Ruthenium	Ru	=	101·7.
	45	Rhodium	Rh	=	102·9.
	46	Palladium	Pd	=	106·7.
{	76	Osmium	Os	=	190·9.
	77	Iridium	Ir	=	193·1.
	78	Platinum	Pt	=	195·2.

Occurrence.

The two triads of transition-elements set out above form a group of six "precious metals," which resemble one another so closely that their separation from one another is not readily accomplished, although it is not so difficult as in the case of the elements of the rare earths. They are associated together in the crude platinum ores of Russia and California, which consist mainly of metallic platinum with about 5 to 10 per cent. of iron, about 5 per cent. of the other platinum metals, and perhaps 1 per cent. each of gold and copper. The compounds found as minerals are the sulphide, Rh_2S_2, and the arsenide, $PtAs_2$, isomorphous with pyrites, FeS_2.

Classification.

(*a*) A remarkable feature of this group of elements is the complete contrast between their properties and those of the transition-elements of the iron group. Thus, (i) the six platinum metals are constantly associated together in Nature, but they do not occur in iron ores in the same way in which silver and gold occur in copper ores and cadmium in zinc ores ; (ii) their physical properties are quite distinct, *e.g.*, none of the platinum metals possesses magnetic properties ; (iii) their valencies and chemical properties are dissimilar, mainly on account of the fact that all the platinum metals give quadrivalent compounds, which are indeed a dominant characteristic of the group, but have no clear analogy in the case of iron, cobalt, and nickel.

(*b*) In spite of the striking contrast between these elements and those of the iron triad with which they are associated in column VIII of Table 61, there is a very marked resemblance between the corresponding pairs of elements in the palladium and platinum triads,

44. Ruthenium,	45. Rhodium,	46. Palladium,
76. Osmium,	77. Iridium,	78. Platinum,

and the special features of these three pairs of elements recall in several instances the points of contrast between

26. Iron, 27. Cobalt, 28. Nickel.

(i) *Ruthenium* and *osmium* alone form volatile **tetroxides,** RuO_4, OsO_4; these are soluble in water, but devoid of acid properties, and correspond with the hypothetical oxide, MO_4, which is usually written at the head of this column in the periodic classification of the elements. They are also unique in forming nitroso-compounds such as

$$K_2[Ru.NO.Cl_5] \text{ and } K_2[Os.NO.Cl_5];$$

compare potassium nitroprusside, $K_2[Fe.NO.5CN]$.

(ii) *Rhodium* and *iridium* agree with one another in the importance of their tervalent compounds, *e.g.*, they are the only elements in these two triads which form alums such as

$$KRh(SO_4)_2,12H_2O, \quad KIr(SO_4)_2,12H_2O.$$

They also agree with one another in forming a large number of co-ordinated compounds (p. 797) analogous to the cobalticyanides, cobaltinitrites, and cobalt-ammines, in which again the metal is tervalent, *e.g.*,

$K_3RhC_6N_6$	$K_3IrC_6N_6$
$K_3Rh(NO_2)_6$	$K_3Ir(NO_2)_6$
$RhCl_3,6NH_3$ or $[Rh.6NH_3]Cl_3$	$IrCl_3,6NH_3$ or $[Ir.6NH_3]Cl_3$
$RhCl_3,5NH_3$ or $[Rh.5NH_3.Cl]Cl_2$	$IrCl_3,5NH_3$ or $[Ir.5NH_3.Cl]Cl_2$.

(iii) *Palladium* and *platinum* agree with one another in forming, in addition to a univalent chloride, mainly bivalent and quadrivalent salts, *e.g.*, their chlorides are

$PdCl$,	$PdCl_2$,	$PdCl_4$,
$PtCl$,	$PtCl_2$,	$PtCl_4$.

Many of these compounds are isomorphous with one another, *e.g.*,

K_2PdCl_4	$K_2PdC_4N_4$	K_2PdCl_6
K_2PtCl_4	$K_2PtC_4N_4$	K_2PtCl_6.

They also form co-ordinated compounds in which *four* radicals are clustered round the metallic atom, *e.g.*,

Palladium Compounds.	*Platinum Compounds.*
$2KCN,PdC_2N_2,3H_2O$ or $K_2[Pd.4CN],3H_2O$	$2KCN,PtC_2N_2,12H_2O$ or $K_2[Pt.4CN],12H_2O$
$2KCNS,Pd(CNS)_2$ or $K_2[Pd.4CNS]$	$2KCNS,Pt(CNS)_2$ or $K_2[Pt.4CNS]$
$2KNO_2,Pd(NO_2)_2$ or $K_2[Pd.4NO_2]$	$2KNO_2,Pt(NO_2)_2 2H_2O$ or $K_2[Pt.4NO_2]2H_2O$
$PdCl_2,4NH_3$ or $[Pd.4NH_3]Cl_2$	$PtCl_2,4NH_3$ or $[Pt.4NH_3]Cl_2$
$PdCl_2,2NH_3$ or $[Pd.2NH_3.2Cl]$	$PtCl_2,2NH_3$ or $[Pt.2NH_3.2Cl]$
$PdC_2N_2,2NH_3$ or $[Pd.2NH_3.2CN]$	$PtC_2N_2,2NH_3$ or $[Pt.2NH_3.2CN]$.

These are in addition to compounds of the more usual type in which six radicals are shown inside the brackets, as in

$$K_2[PtCl_6] \qquad K_2[PdCl_6] \qquad K_2[Pt.6CNS].$$

Palladium and platinum also share the marked catalytic activity which has already been noticed as a special property of nickel.

78. Platinum. Pt = 195·2.

Classification.

Platinum, the typical element of these two triads of transition elements, is a noble metal which resembles gold in its general properties, *e.g.*, in its resistance to the action of oxygen and sulphur, and of oxidising acids such as nitric acid and concentrated sulphuric acid, as well as in its susceptibility to attack by chlorine and by chlorinating agents, such as aqua regia.

$$Au + 4HCl + HNO_3 = HAuCl_4 + NO + 2H_2O$$
$$3Pt + 18HCl + 4HNO_3 = 3H_2PtCl_6 + 4NO + 8H_2O.$$

In each case the product of the action of aqua regia is not a simple chloride but a chloro-acid, from which salts such as $NaAuCl_4$ and K_2PtCl_6 can be derived. In each case also a chloride of lower valency is known, and all the chlorides are decomposed by heat, giving a residue of spongy metal; the metals can also be precipitated from solution by reducing agents such as ferrous sulphate. Mendeléeff was so impressed by this resemblance between platinum and gold that he showed gold in two places in his table, *i.e.*, as a member of the platinum group as well as in column I.

Metallic Platinum.

(*a*) *Occurrence.*—Although alloys containing platinum have been used from very early times, platinum was first recognised in the sixteenth century as a white infusible metal occurring in the gold-bearing sands of Central America, and was distinguished as "platina," or small silver (*platina*, diminutive of Spanish *plata*, silver). Platinum

It is a greenish-grey powder, and like aurous chloride is insoluble in water. It is a highly unsaturated compound and forms a large number of addition-compounds, *e.g.*, $PtCl_2,PCl_3$, prepared from Pt and PCl_5, and $PtCl_2,2PCl_3$, formed by further combination with phosphorus trichloride. Carbon monoxide at 250° gives $PtCl_2,COCl_2$, $PtCl_2,CO$, $PtCl_2,2CO$, and $2PtCl_2,3CO$; the most stable of these compounds decomposes when heated at 300°, as shown in the equation

$$PtCl_2,CO = Pt + COCl_2,$$

whilst water gives metallic platinum, carbon dioxide, and hydrogen chloride. The CHLOROPLATINITES, or PLATINOCHLORIDES, which are salts of chloroplatinous acid, H_2PtCl_4, are prepared by reducing the platinichlorides, *e.g.*,

$$K_2PtCl_6 + Cu_2Cl_2 = K_2PtCl_4 + 2CuCl_2;$$

the product, **potassium platinochloride,** K_2PtCl_4, is much more soluble than the platinichloride, and crystallises from hot water in fine rose-coloured needles; by boiling a very dilute solution of the platinochloride for some days, a yellow precipitate of **platinum monochloride,** PtCl, is formed. The **ammonium salt** is soluble in water but the **silver** and **lead salts** are insoluble. **Chloroplatinous acid,** H_2PtCl_4, can be prepared by precipitating the **barium salt** with sulphuric acid or the potassium salt with chloroplatinic acid,

$$\underset{\text{(soluble)}}{K_2PtCl_4} + \underset{\text{(soluble)}}{H_2PtCl_6} = \underset{\text{(insoluble)}}{K_2PtCl_6} + \underset{\text{(soluble)}}{H_2PtCl_4},$$

but is partly hydrolysed when the solution is evaporated. The **fluoride,** PtF_2, prepared by direct combination of platinum and fluorine at a red heat, is soluble in water, and is decomposed by heating strongly.

Platinous hydroxide, $Pt(OH)_2$, is prepared by boiling equivalent quantities of sodium hydroxide and potassium platinochloride until neutral,

$$K_2PtCl_4 + 2NaOH = 2KCl + 2NaCl + Pt(OH)_2.$$

It retains its water up to 400°, but is decomposed into the metal and its dioxide by boiling with potassium hydroxide. Careful ignition converts it into the grey or violet **monoxide,** PtO. The corresponding **monosulphide,** PtS, prepared by direct combination of spongy platinum with sulphur, is a green powder, which leaves a residue of platinum when heated in air.

Platinic Salts.

Platinic chloride, $PtCl_4$, can be prepared from its elements by direct combination, but decomposes again above 500°. It is also formed from dry chloroplatinic acid, H_2PtCl_6, by heating at 165° in hydrogen chloride or at 369° in a current of chlorine,

$$H_2PtCl_6 = PtCl_4 + 2HCl.$$

Aqueous chloroplatinic acid can be converted into platinic chloride by precipitating the silver salt and decomposing this with hot water,

$$Ag_2PtCl_6 = PtCl_4 + 2AgCl;$$

on evaporating the solution over sulphuric acid, the **pentahydrate,** $PtCl_4,5H_2O$, is deposited in red crystals.

Chloroplatinic acid, H_2PtCl_6, prepared by dissolving platinum in aqua regia, and removing the excess of nitric acid by evaporation with hydrochloric acid, separates from water in brownish-red deliquescent prisms of the **hexahydrate,** $H_2PtCl_6,6H_2O$; evaporation with aqua regia produces a **nitrosoplatinic chloride,** $PtCl_4,2NOCl$, or $(NO)_2PtCl_6$, which crystallises in orange cubes, but liberates nitric oxide when dissolved in water. The CHLOROPLATINATES or PLATINICHLORIDES have long been known on account of the sparing solubility (1·1 per cent. at 20°) of **potassium platinichloride,** K_2PtCl_6, which is used in detecting and estimating potassium, as well as of the **ammonium**, **rubidium,** and **cæsium salts,** which dissolve to the extent of only 0·66, 0·14, and 0·07 per cent. at 20°.

Platinic acid, $PtO_2,4H_2O$, or $H_2Pt(OH)_6$, compare H_2PtCl_6, is formed as a white precipitate on boiling platinic chloride with potassium hydroxide. By heating it gently **platinic oxide,** PtO_2, is obtained as a black powder. The hydrated compound dissolves in alkalies to form PLATINATES, *e.g.*, **potassium platinate,** $K_2Pt(OH)_6$, which are isomorphous with the stannates, *e.g.*, $K_2Sn(OH)_6$ (p. 688).

Platinic sulphide, PtS_2, is a grey powder formed by heating ammonium platinichloride with sulphur at a red heat or by precipitating potassium platinichloride with sulphuretted hydrogen at 90°.

Co-ordinated Compounds.

The co-ordinated compounds of platinum are of two kinds containing either four or six co-ordinated groups.

(*a*) *Four Groups.*

Potassium platinochloride, K_2PtCl_4, has already been described above; the **acid** is known in solution, but one chlorine atom is replaced by hydroxyl when it is evaporated even in a vacuum. The PLATOSAMMINES derived from platinous chloride include

$PtCl_2,NH_4Cl,NH_3,H_2O$ or $[Pt.NH_3.3Cl]NH_4,H_2O$
$PtCl_2,2NH_3$ or $[Pt.2NH_3.2Cl]$
$PtCl_2,3NH_3$ or $[Pt.3NH_3.Cl]Cl$
$PtCl_2,4NH_3,H_2O$ or $[Pt.4NH_3]Cl_2,H_2O$.

The **diammine** is known in two isomeric forms. The **tetrammine** has been known since 1826, under the name of "Magnus' green salt," as a platinochloride which has the same empirical composition, $PtCl_2,2NH_3$, as the two diammines, but this is now formulated as $[Pt.4NH_3]PtCl_4$, compare $MgPtCl_4$.

Potassium platinocyanide, $K_2PtC_4N_4$, is prepared by boiling ammonium platinichloride with potassium hydroxide and cyanide until ammonia is no longer liberated ; it is also formed when spongy platinum is dissolved in potassium cyanide,

$$2Pt + 8KCN + O_2 + 2H_2O = \underset{\text{Potassium platinocyanide}}{2K_2PtC_4N_4} + 4KOH;$$

compare

$$4Au + 8KCN + O_2 + 2H_2O = \underset{\text{Potassium aurocyanide}}{4KAuC_2N_2} + 4KOH.$$

It dissolves readily in water, and separates from it in yellow prisms. It combines with chlorine to form **potassium chloroplatinicyanide,** $K_2PtC_4N_4Cl_2$, instead of losing potassium, like potassium ferrocyanide or potassium manganate. The **barium salt,** $BaPtC_4N_4$, is used in fluorescent screens for detecting *X*-rays.

Potassium platinothiocyanate, $K_2Pt(CNS)_4$, is prepared in minute red prisms by dissolving the platinochloride and thiocyanate in water,

$$K_2PtCl_4 + 4KCNS = 4KCl + K_2Pt(CNS)_4.$$

The **acid** can be prepared by precipitating the lead salt with dilute sulphuric acid, but has not been isolated in a pure state.

Potassium platinonitrite, $K_2Pt(NO_2)_4$, is prepared in glistening prisms, by mixing solutions of potassium platinochloride and nitrite,

$$K_2PtCl_4 + 4KNO_2 = K_2Pt(NO_2)_4 + 4KCl.$$

It exhibits all the typical properties of a co-ordinated compound, since the double-nitrite is not decomposed by acids, which merely liberate the free **acid,** $H_2Pt(NO_2)_4$, and the platinum is not precipitated by alkalies or by sulphuretted hydrogen. It behaves, however, as an unsaturated compound and combines with $2H_2O, Cl_2, Br_2, HCl$ and N_2O_4. The **silver salt,** $Ag_2Pt(NO_2)_4$, crystallises from hot water in glistening yellow prisms.

(*b*) *Six Groups.*

These compounds include the co-ordinated chlorides, hydroxides and ammines of quadrivalent platinum; the platinicyanides and platininitrites, however, are still unknown. The diammine, $PtCl_4,2NH_3$, may have either four or six co-ordinated groups, as set out in the table below.

	$PtCl_4,2KCl$	or	$[Pt.6Cl]K_2$.
	$Pt(OH)_4,2KOH$	or	$[Pt.6OH]K_2$.
	$PtCl_4,KCl,NH_3$	or	$[Pt.NH_3.5Cl]K$.
	$\{ PtCl_4,2NH_3$	or	$[Pt.2NH_3.2Cl]Cl_2$,
	$\} PtCl_4,2NH_3$	or	$[Pt.2NH_3.4Cl]$.
	$PtCl_4,3NH_3$	or	$[Pt.3NH_3.3Cl]Cl$.
	$PtCl_4,4NH_3$	or	$[Pt.4NH_3.2Cl]Cl_2$,
also	$[Pt.4NH_3.2Cl]PtCl_4$	and	$[Pt.4NH_3.2Cl]PtCl_6$.
	$PtCl_4.6NH_3$	or	$[Pt.6NH_3]Cl_4$.

Detection and Estimation of Platinum.

Platinum is usually separated as **ammonium platinichloride,** $(NH_4)_2PtCl_6$, and weighed as metal after igniting this salt. In qualitative analysis the **disulphide,** PtS_2, is precipitated by sulphuretted hydrogen, and is associated with the sulphides of arsenic, antimony, tin and gold.

The atomic weight of platinum has been determined by estimating the metal and the halogen in K_2PtCl_6, K_2PtBr_6, $(NH_4)_2PtCl_6$, and $(NH_4)_2PtBr_6$.

44. **Ruthenium.** Ru = 101·7.

Ruthenium is present in platinum ores and in the insoluble residue of "osmiridium" which is left when crude platinum is dissolved in aqua regia; it is also found as the sulphide, Ru_2S_3. It is a heavy metal of density 12·0 and is extremely hard. Its melting-point is about 2450°; it is, therefore, only less infusible than osmium in this group of metals. The molten metal absorbs oxygen, but liberates it again as it cools, giving rise to "spitting" as in the case of silver (p. 847) and platinum. Ruthenium is remarkable for its wide range of valencies, in which respect it resembles manganese, although a determination of its atomic number proves that it is not a homologue of this element.

(*a*) *Chlorides of Ruthenium.*—**Ruthenium trichloride,** $RuCl_3$, is formed by the action of chlorine and carbon monoxide on the metal; it forms **double salts** of the type K_2RuCl_5, compare K_2MnCl_5; this double salt is converted by nitric acid into a **nitroso-compound,** $K_2RuCl_5(NO)$ or $K_2[Ru.NO.5Cl]$, compare potassium nitroprusside, $K_2[Fe.NO.5CN]$. The yellow solution of the trichloride becomes blue by the action of sulphuretted hydrogen; this solution probably contains **ruthenium dichloride,** $RuCl_2$ (compare chromous chloride, $CrCl_2$, p. 737), since it gives a **double salt,** $3CsCl,RuCl_2,2H_2O$ or $Cs_3RuCl_5,2H_2O$, with cæsium chloride. Ruthenium tetrachloride, $RuCl_4$, has also not been isolated, but **potassium ruthenichloride,** K_2RuCl_6, can be prepared in reddish-brown, sparingly soluble crystals, by fusing ruthenium with potassium hydroxide and nitrate, dissolving in cold water, and adding hydrochloric acid.

(*b*) *Oxides of Ruthenium.*—**Ruthenium dioxide,** RuO_2 (compare MnO_2), is obtained by roasting the disulphide or the sulphate in air, or by burning the crude osmiridium alloy in an oxidising atmosphere at 1000°. It condenses in small, hard crystals, with a green metallic lustre; these are isomorphous with cassiterite, SnO_2, and with rutile, TiO_2.

Ruthenium tetroxide, RuO_4, resembles sulphur trioxide or perchloric acid in some of its properties. It is obtained by passing chlorine into a solution of sodium ruthenate, prepared by fusing the metal with sodium peroxide. Although less volatile than the corresponding compound of osmium, it distils out readily from the solution and can be condensed in a receiver. It melts at 25°, and boils at 42° under 20 mm. pressure, but decomposes to the dioxide when heated at 106°. It is a powerful oxidising agent and explodes violently with alcohol.

Potassium ruthenate, K_2RuO_4,H_2O (compare K_2MnO_4), is prepared by igniting the metal with potassium hydroxide and potassium nitrate; it gives a red solution in water and separates from it in black crystals with a green metallic lustre (compare the physical properties of potassium permanganate). When acted on by chlorine it gives **potassium perruthenate,** $KRuO_4$ (compare $KMnO_4$), a green salt which separates from water in black crystals; these are, however, not isomorphous with those of potassium permanganate.

(c) *Sulphides and Sulphate.*—**Ruthenium sesquisulphide,** Ru_2S_3, is found as a mineral. A mixture of sulphides, including RuS_2 and RuS_3, is produced by precipitating potassium ruthenichloride, K_2RuCl_6, with sulphuretted hydrogen. On dissolving these sulphides in nitric acid, **ruthenic sulphate,** $Ru(SO_4)_2$, is formed, and separates as a deliquescent reddish-yellow residue on evaporating the solution.

(d) *Co-ordinated Compounds.*—These include the RUTHENIOCYANIDES, *e.g.*, $H_4[RuC_6N_6]$ and $K_4[RuC_6N_6],3H_2O$, in which the ruthenium is bivalent, and the NITROSOCHLORIDES, etc., *e.g.*, $K_2[Ru.NO.5Cl]$, in which the metal is tervalent.

45. **Rhodium,** Rh = 102·9, is a heavy metal of density 12·5; it melts at 1950° and "spits" on cooling. An alloy containing 10 per cent. of rhodium and 90 per cent. of platinum is used for thermo-junctions (compare iridium, p. 823). Rhodium differs from ruthenium mainly in the disappearance of the higher valencies and with them of the acid properties which are seen in the ruthenates and perruthenates. It forms a few bivalent and quadrivalent compounds, *e.g.*, RhO, RhS and $RhCl_2$, and RhO_2, but almost all its important compounds are tervalent.

Rhodium trichloride, $RhCl_3$, forms double salts such as $Na_3RhCl_6,9H_2O$ and K_2RhCl_5, and **ammines** such as $RhCl_3,6NH_3$ or $[Rh.6NH_3]Cl_3$ and $RhCl_3,5NH_3$ or $[Rh.5NH_3.Cl]Cl_2$. **Rhodium sulphate,** $Rh_2(SO_4)_3,12H_2O$, forms a series of alums such as $KRh(SO_4)_2,12H_2O$. **Potassium rhodicyanide,** $K_3RhC_6N_6$ (compare potassium ferricyanide), differs from potassium iridicyanide, $K_3IrC_6N_6$, in that it is decomposed by acetic acid, depositing the **tricyanide,** RhC_3N_3. **Potassium rhodinitrite,** $K_3Rh(NO_2)_6$, is colourless and almost insoluble in water; it can be used for the separation of rhodium.

46. **Palladium,** Pd = 106·7, was discovered by Wollaston in 1804. It is a silvery metal of density 12·1 and melts at 1549°, the lowest temperature of all the platinum metals. The metal, which shows many points of resemblance to platinum, is remarkable for its power of absorbing hydrogen (p. 91), of which it may take up nearly 900 times its own volume, but almost the whole of this can be removed by pumping off the gas, even at atmospheric temperatures. The metal retains its metallic appearance, but expands considerably during the absorption. The composition of the product, which perhaps contains a **hydride** in solid solution in the metal, corresponds approximately with the formula Pd_3H_2. It is a powerful reducing agent, which interacts with chlorine and oxygen even in the dark,

converts mercuric chloride into mercurous chloride, ferric salts into ferrous salts, ferricyanides into ferrocyanides, chlorates into chlorides, arsenious oxide into arsenic, sulphur dioxide into hydrogen sulphide, and potassium nitrate into potassium nitrite and ammonia. In presence of oxygen and water, however, it *oxidises* carbon monoxide to carbon dioxide, perhaps as shown in the equation

$$PdH_2 + O_2 + CO = Pd + H_2O + CO_2;$$

in the same way, it will oxidise benzene, C_6H_6, to phenol, $C_6H_5\cdot OH$, and toluene, $C_6H_5\cdot CH_3$, to benzoic acid, $C_6H_5\cdot CO_2H$.

When heated in oxygen, palladium oxidises to the **monoxide,** PdO, but this dissociates again above 877°, when the dissociation pressure rises to 760 mm.; the absorption of oxygen by finely-divided palladium is probably due to oxidation of occluded hydrogen, or to a superficial oxidation of metal to the monoxide, since the oxygen cannot be pumped off again even at a red heat. Palladium burns with incandescence in sulphur vapour to the **monosulphide,** PdS. With the exception of the **monochloride,** PdCl, prepared by fusing the dichloride, $2PdCl_2 = 2PdCl + Cl_2$, compare $AuCl_3 = AuCl + Cl_2$, almost all its compounds are bivalent or quadrivalent. The bivalent compounds include **palladious chloride,** $PdCl_2,2H_2O$, prepared in red crystals by heating the monosulphide, PdS, in dry chlorine; this forms **double salts** such as K_2PdCl_4, and also combines with phosphorus trichloride to form the compounds $PdCl_2,PCl_3$ and $PdCl_2,2PCl_3$. At temperatures below 260° the anhydrous chloride combines with carbon monoxide to form **carbonyl compounds** such as $PdCl_2,CO$ and $PdCl_2,2CO$ (compare iron, p. 791), but in dilute aqueous solutions acidified with hydrochloric acid it is reduced to metal by carbon monoxide and can be used to estimate traces of this gas by a colorimetric method. Palladium also forms a bivalent **sulphate,** $PdSO_4,2H_2O$, **nitrate,** $Pd(NO_3)_2$, **cyanide,** PdC_2N_2, and **double cyanides** such as $K_2PdC_4N_4$. **Palladic chloride,** $PdCl_4$, is not known, but **double salts** such as K_2PdCl_6 and $(NH_4)_2PdCl_6$ can be prepared, *e.g.*, by adding potassium chloride or ammonium chloride to a solution of the metal in aqua regia.

76. **Osmium,** Os = 190·9.—When platinum ores are dissolved they usually leave behind a residue of OSMIRIDIUM, which is very resistant to attack by acids. This is an alloy of osmium and iridium, the two metals with the highest known density and with the highest melting-points in the platinum group.

Osmium has the highest density (22·5) recorded for any substance. Its melting-point, 2700°, is higher than that of any other metal of the platinum group, although lower than those of tantalum and tungsten; but its use as a filament in incandescent lamps is said to have been abandoned on account of the risk arising from the ready combustion of the metal to a poisonous oxide, if the bulb should break.

Although associated closely with platinum and iridium as a member of the platinum triad, osmium is a base metal, which oxidises at atmospheric temperatures when finely divided, and at 200° to 400° when in a compact form; it is, however, dissolved by hydrochloric

acid only when oxygen is present. Osmium is also notable for the fact *that in nearly all its compounds it appears as a constituent of the acid* radical, and thus assumes many of the functions of a non-metal; thus the osmates, such as K_2OsO_4, may be compared with the sulphates, such as K_2SO_4, or with the selenates, such as K_2SeO_4, as well as with the ruthenates, such as K_2RuO_4. The osmyl salts, in which the oxide OsO_2 plays the part of a metal, may be compared with compounds such as MoO_2F_2, WO_2F_2, $UrO_2(NO_3)_2$ in the chromium family, or with $VO(SO_4)$, $VOCl_3$, $CbOF_3$, etc., in the vanadium family.

(*a*) *Oxides.*

Osmium resembles ruthenium and differs from all the other platinum metals in forming a volatile **tetroxide,** OsO_4, sometimes incorrectly called "osmic acid," by means of which it can be separated with exceptional ease from the other elements of the group. This oxide is formed by direct combustion, the volatility of the oxide being perhaps responsible for the ready oxidation of the metal. It is also formed by oxidation of the metal by nitric acid or by strong sulphuric acid. It sublimes in glistening needles which become soft and waxy when warm, and boils at 100° to a vapour of normal density. The vapour has an odour which resembles that of chlorine or iodine, and is extremely irritating and poisonous in its properties. It dissolves in water, but the solution does not redden litmus paper. It is a powerful oxidising agent and deflagrates like nitre on red-hot charcoal. It is also reduced in solution by organic compounds and is used in this way as a stain.

Osmium trioxide, OsO_3, is unknown, but the tetroxide gives with alkalies, in presence of a reducing agent such as alcohol, a series of OSMATES derived from this oxide, *e.g.*, **potassium osmate,** $K_2OsO_4,2H_2O$ (compare K_2RhO_4 and K_2MnO_4), and **sodium osmate,** Na_2OsO_4. **Barium osmate** is insoluble in water. Potassium osmate is also formed by atmospheric oxidation when osmium is attacked by fused potassium hydroxide; when evaporated on a water-bath it is hydrolysed, and **osmic acid,** H_2OsO_4, is produced as a black deposit. The oxides OsO_2, Os_2O_3, and OsO have been prepared from the salts corresponding with these bases.

(*b*) *Chlorides, etc.*

Osmium forms an unstable bluish-black **dichloride,** $OsCl_2$, a purple **trichloride,** $OsCl_3$, which is known as a **trihydrate,** $OsCl_3,3H_2O$, and in the form of OSMOCHLORIDES such as **potassium osmochloride,** $K_3OsCl_6,3H_2O$, and a yellow **tetrachloride,** $OsCl_4$, prepared by heating the metal in chlorine, which forms OSMICHLORIDES such as **potassium osmichloride,** K_2OsCl_6. Osmium also forms OSMOCYANIDES, *e.g.*, $K_4OsC_6N_6,3H_2O$, from which the free acid, $H_4OsC_6N_6$, *can be prepared in colourless scales by the action of fuming* hydrochloric acid.

(*c*) *Nitrogen Compounds.*

(i) By the action of ammonia and potassium hydroxide on osmium tetroxide, **potassium osmiate,** $KOsNO_3$, *is produced in orange-yellow crystals,*

$$OsO_4 + KOH + NH_3 = KOsNO_3 + 2H_2O.$$

Its constitution is not certain, but since it is reduced by stannous chloride and hydrochloric acid to the **amide,** $K_2[Os.NH_2.Cl_5]$, it is perhaps a nitroso-compound, *e.g.*, NO·OsO·OK.

(ii) By the action of nitric oxide and potassium nitrite on osmium tetroxide, **potassium osmyl nitrite,** $K_2OsO_2(NO_2)_4$, or $K_2[OsO_2.4NO_2]$, is produced in black needles. This salt may perhaps be compared with the palladionitrite, $K_2Pd(NO_2)_4$, and the platinonitrite, $K_2Pt(NO_2)_4$, the osmyl radical, OsO_2, acting the part of a metal just like the vanadyl radical, VO, or the uranyl radical, UO_2.

(iii) By acting on the preceding compound with concentrated hydrochloric acid, the **nitrosochloride,** $2KCl,OsCl_3,NO$, or $K_2[Os.NO.5Cl]$, is produced in red crystals isomorphous with the corresponding ruthenium salt, $K_2[Ru.NO.5Cl]$.

77. **Iridium,** Ir = 193·1.—Some platinum ores contain a large proportion of iridium, in the form of osmiridium, an alloy of Os and Ir which is very resistant to attack by acids and remains behind when the platinum is dissolved in aqua regia. The ready oxidation of osmium and the acid properties of its oxide make the separation of these two metals comparatively easy.

Iridium is almost equal to osmium in its density, 22·4, and in its melting-point, 2350°. An alloy of iridium with nine parts of platinum is extremely hard, does not alter in the air, and takes a very fine polish; it has been used for standards of length, for electrodes in electrolysis, and for pyrometer wires (compare rhodium, of which it is the homologue). Finely-divided iridium is even more active than platinum as a catalyst in promoting oxidation; it oxidises in air and dissolves in aqua regia, but the massive metal is not attacked.

As in the case of rhodium, the most important salts of iridium are tervalent. They include **iridium trichloride,** $IrCl_3$, and double salts such as **potassium iridiochloride,** $K_3IrCl_6,3H_2O$. An insoluble **dichloride,** $IrCl_2$, and a soluble **iridium tetrachloride,** $IrCl_4$, have also been prepared, together with double salts such as **potassium iridiochloride**, K_2IrCl_6, isomorphous with K_2PdCl_6 and K_2PtCl_6. Iridium also forms a **sesquisulphate,** $Ir_2(SO_4)_3$, and a series of **alums** of the type $KIr(SO_4)_2,12H_2O$. There is also a **double sulphate,** $K_3Ir(SO_4)_3,H_2O$, analogous to the double sulphates of the rare earths, *e.g.*, $K_3Ce(SO_4)_3$.

The *co-ordinated compounds* of iridium include the AMMINES of the bivalent chloride, $IrCl_2$, which may be written with four co-ordinated groups, *e.g.*,

$IrCl_2,2NH_3$ or $[Ir.2NH_3.Cl_2]$
$IrCl_2,4NH_3$ or $[Ir.4NH_3]Cl_2$,

whilst the AMMINES derived from the trichloride, or from quadrivalent compounds of iridium, contain six co-ordinated groups, *e.g.*,

$IrCl_3,5NH_3$ or $[Ir.5NH_3.Cl]Cl_2$
$IrCl_3,6NH_3$ or $[Ir.6NH_3]Cl_3$
$IrCl_2(NO_3)_2,4NH_3$ or $[Ir.4NH_3.Cl_2](NO_3)_2$.

The complex chlorides, cyanides, and nitrites contain six co-ordinated groups, whatever the valency of the metal may be, *e.g.*,

	Bivalent.	*Tervalent.*	*Quadrivalent.*
Chlorides . . .	—	K_3IrCl_6	K_2IrCl_6
Cyanides . . .	$K_4IrC_6N_6$	$K_3IrC_6N_6$	—
Nitrites . . .	—	$K_3Ir(NO_2)_6$	—

CHAPTER XLIII

THE COINAGE METALS

Atomic Number.	*Element.*	*Symbol.*		*Atomic Weight.*
29	Copper	Cu	=	63·57
47	Silver	Ag	=	107·88
79	Gold	Au	=	197·2

Classification.

The three elements copper, silver, and gold form a natural group of metals which have been employed from very early times as the almost universal basis of systems of coinage. The selection of these three metals is based on the facts (i) that they are sufficiently plastic under pressure to be "struck" between dies; (ii) that they are sufficiently hard, or become sufficiently hard during coining, if necessary after alloying with small quantities of other metals, to withstand ordinary wear; (iii) that they are sufficiently tough not to be broken easily by a blow; (iv) that they are not readily attacked either by air or by water and therefore remain clean and bright during use; and finally (v) that their occurrence in Nature is so graded as to establish a convenient scale of values in coins of similar size.

In Mendeléeff's table these metals were associated with the metals of the alkalies, and sodium was placed at the head of the group. Later writers have sought to justify this grouping, by directing attention to the fact that the coinage metals, like the metals of the alkalies, form univalent salts, although these differ from the salts of the alkalies not only in their properties, but probably also in their molecular formulæ, thus,

{Sodium chloride,	$NaCl$	soluble in water
{Potassium chloride,	KCl	soluble in water.
{Cuprous chloride,	Cu_2Cl_2	insoluble in water
{Silver chloride,	$(Ag\ Cl)_n$	insoluble in water.

The wide divergence between the coinage metals and the metals of the alkalies was, however, clearly recognised by Mendeléeff, who placed the coinage metals in two alternative positions, namely, in column I with the elements of the alkalies, but also in column VIII, where copper was associated with nickel, silver with palladium, and

gold with platinum. This alternative grouping is very suggestive, and directs attention, for instance, to the use of copper and nickel in electro-plating and to the use as alternatives in jewelry of the two noble metals gold and platinum, as well as to other points of resemblance to which attention is directed in describing the individual metals below.

Physical Properties of the Coinage Metals.

The physical properties of the elements are shown in the following table :

TABLE 90.—PHYSICAL PROPERTIES OF THE COINAGE METALS.

	Density.	*Melting-point.*	*Electrical Conductivity.**	*Thermal Conductivity.*
Cu . .	8·94	1083°	64 × 10^4	0·9 at 18°
Ag . .	10·5	960°	67	1·0
Au . .	19·3	1062°	45	0·7

The three metals are of high density and are remarkable in that they all melt in the neighbourhood of 1000°. It is of interest, as indicating

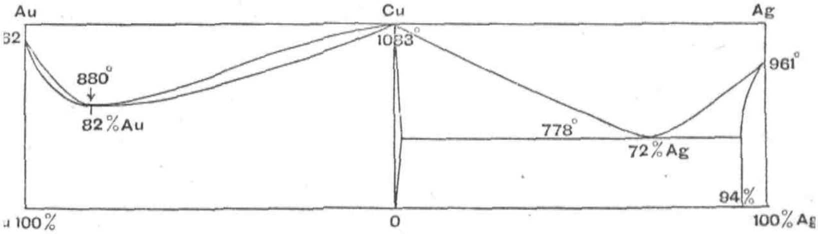


FIG. 276.—FREEZING-POINT CURVES FOR ALLOYS OF COPPER, SILVER, AND GOLD.

the close relationship of the coinage metals to the elements of the iron, palladium, and platinum triads, to notice that whilst copper forms a complete series of solid solutions with nickel (Fig. 273, p. 804), silver with palladium, and gold with platinum (Fig. 67b, p. 181), these elements being immediate neighbours in the three series of transition-elements, the solid solutions of copper and gold give a freezing-point curve (Fig. 276) which passes through a minimum, just like vanadium and iron, chromium and cobalt, manganese and nickel, which are three places removed from one another in the transition series, or manganese and copper (Fig. 256, p. 754), which are four places removed. Finally, copper and silver, which are consecutive members of the group of coinage metals, actually form an eutectic alloy, in which the silver takes up only 6 per cent. of copper and the copper only about 1 per cent. of silver (Fig. 276). Silver and gold are, however, completely isomorphous with one another (Fig. 67a, p. 181).

Reciprocal ohms per cm. cube at 0°.

Chemical Properties of the Coinage Metals.

(*a*) *Valency.*—The distribution of valencies amongst the coinage metals may be illustrated by writing down the formulæ of the chlorides, as follows :

	Univalent.	*Bivalent.*	*Tervalent.*
Copper . . .	Cu_2Cl_2	$CuCl_2$	—
Silver . . .	AgCl	—	—
Gold . . .	AuCl	—	$AuCl_3$

The univalent compounds appear to be typical of the group, the members of which include the first element of the second octave in each of the long periods IV, V, and VI. Copper shows in addition the bivalency of nickel and zinc, its immediate neighbours in the periodic classification; its two valencies agree in a curious way with those of mercury in column II. The tervalency of gold corresponds with that of iridium and thallium, two metals which are removed two places from it in the periodic classification of the elements; its general properties, however, resemble more closely those of platinum, its immediate neighbour in the transition series, although the valencies of this element are usually 2 and 4, instead of 1 and 3.

(*b*) *Oxidation.*—The coinage metals show an interesting gradation of chemical properties from the base metal, copper, which oxidises readily when heated in air and burns with incandescence in oxygen when finely divided, to the noble metal, gold, which does not oxidise in air and of which the oxide is easily decomposed by heating. Silver occupies an intermediate position, since, although it is not converted into an oxide by heating in the air, it absorbs oxygen when melted and sets it free again when the metal becomes solid.

(*c*) *Precipitation and Decomposition of Oxides.*—Copper burns in air to the black oxide, CuO, but when this is heated strongly it loses half its oxygen and is converted into the red oxide, Cu_2O. Silver oxide can be prepared artificially by precipitation from a silver salt by means of an alkali, but it is not a very stable compound, and its decomposition by heat has been used in the preparation of pure oxygen. In the case of gold, the oxide can be prepared in a similar manner by precipitation from a salt of gold with caustic soda or caustic potash, but when ammonia is used an explosive compound known as FULMINATING GOLD, $Au_2O_3,4NH_3$ (compare mercuric oxide, p. 886), is produced which yields metallic gold, nitrogen, and water vapour when detonated.

(*d*) *Action of Acids.*—The metals of this group do not dissolve in dilute hydrochloric or in dilute sulphuric acid, but copper and silver will dissolve in oxidising acids, *e.g.*, in dilute nitric acid or in concentrated sulphuric acid, liberating oxides of nitrogen or sulphur dioxide instead of hydrogen; copper will, however, dissolve also in dilute sulphuric acid in presence of air, and copper and silver are slowly attacked by strong hydrochloric acid. Gold is not soluble in these

acids, but will dissolve in selenic acid (p. 359), which is a more powerful oxidising agent than sulphuric acid, or in a chlorinating agent such as aqua regia or chlorine water; gold is also soluble in solutions of potassium cyanide when air is present.

(*e*) *Action of Sulphur.*—Copper and silver combine readily with sulphur and are generally found in Nature as sulphide ores. Gold, which does not combine directly with oxygen or with sulphur, is generally found in the metallic state, and large quantities of silver and copper also occur in this form.

29. COPPER. Cu = 63·57.

Occurrence.

(*a*) *Native Copper.*—Copper occurs in the native state, sometimes in enormous masses, as in the copper region of Lake Superior, where it forms veins in the red sandstone. Native copper is, however, very difficult to work, and practically the whole of the world's supplies of copper are extracted from sulphide, oxide, carbonate or sulphate ores.

(*b*) *Sulphide ores* include

Cuprous ferric sulphide as COPPER PYRITES or CHALCOPYRITE, $CuFeS_2$, or Cu_2S,Fe_2S_3, or as a mixed sulphide in VARIEGATED COPPER ORE, Cu_3FeS_3, or $Cu_2S,CuFeS_2$;

Cuprous sulphide as COPPER-GLANCE or CHALCOCITE, Cu_2S;

Cupric sulphide as INDIGO COPPER, CuS.

These sulphide ores are the most abundant and are worked even if they contain only 1·5 to 2 per cent. of copper; but they contain numerous impurities (Fe, Pb, As, Bi, Sn), besides earthy substances such as sand and clay. The difficulty experienced in extracting copper from its ores lies principally in the necessity of eliminating completely these foreign substances.

(*c*) *Oxide and Carbonate Ores* include

Cuprous oxide as CUPRITE or RED COPPER ORE, Cu_2O;

Cupric oxide as BLACK COPPER ORE, CuO;

Basic cupric carbonate as the green mineral MALACHITE, $CuCO_3,Cu(OH)_2$, or as the blue mineral AZURITE or CHESSYLITE, $2CuCO_3,Cu(OH)_2$.

(*d*) *Basic Sulphate Ores.*—Although about two-thirds of the world's supply of copper is derived from the sulphide and oxide ores of North America, and mainly from the United States, the largest copper mine in the world is a deposit of **basic cupric sulphate** in South America.

Separation of Copper from its Ores.

(*a*) *Oxide Ores.*—The treatment of the oxide and carbonate in the absence of sulphides is comparatively simple. The ore is crushed and heated to convert the carbonate and hydroxide into oxide, *e.g.*,

$$CuCO_3,Cu(OH)_2 = 2CuO + CO_2 + H_2O.$$

The roasted material is mixed with fuel (anthracite or coke) and a flux to remove earthy material, and heated in a reverberatory furnace, when crude copper is at once obtained,

$$2CuO + C = 2Cu + CO_2.$$

(*b*) *Sulphide Ores.*—The smelting of the sulphide ores involves a long series of processes, the essential features being (i) the elimination of the iron as a slag of ferrous silicate by oxidation and fusion with siliceous material,

$$2FeS + 3O_2 + SiO_2 = Fe_2SiO_4 + 2SO_2,$$

and (ii) the separation of metallic copper from its sulphide by partial oxidation and fusion, just as in the case of lead (p. 690),

$$\begin{aligned} 2Cu_2S + 3O_2 &= 2Cu_2O + 2SO_2 \\ Cu_2S + 2Cu_2O &= 6Cu + SO_2. \end{aligned}$$

In spite of the marked tendency for the iron to oxidise and pass into the slag in preference to the copper, it is impossible to effect a sharp separation of these two metals in one operation. The elimination of the iron is, therefore, effected in two stages, in the first of which oxidation is carried to a point at which some iron still remains as sulphide, thus ensuring that very little copper is lost in the slag; in the second stage, on the other hand, all the iron and some of the copper are oxidised, but the copper which passes into the slag is returned to the process and recovered. The return to the earlier stages of the slags formed in the later stages is a constant feature of the process.

Copper Smelting.

(*a*) *The Welsh Process.*—The principal stages of the WELSH PROCESS of copper smelting as carried out in the Swansea district are as follows :—

(i) *Calcination.*—The ore, consisting of copper pyrites and copper carbonates, with a "gangue" largely composed of silicates and quartz (SiO_2), is mixed, on the results of the assay of the different parcels, so as to contain from 9 to 15 per cent. of copper. It is then calcined in order to oxidise the iron, whilst leaving most of the copper sulphide unchanged. The calcination is effected by burning the ore in heaps, in kilns, in reverberatory furnaces, or finally in rotary furnaces similar to those used in the manufacture of cement (Fig. 238, p. 641).

During the calcination, copper carbonate is converted into copper oxide, ferrous sulphide and ferric sulphide are burnt to oxides of iron, whilst the cuprous sulphide present in the ore remains for the most part unchanged. Sulphur dioxide passes off into a flue and can be used for making sulphuric acid, whilst arsenic is oxidised to arsenious oxide, As_4O_6, and settles as a flue-dust.

(ii) *First Fusion.*—After calcination, the ore is heated in a special MELTING FURNACE or ORE FURNACE, in such a way that the oxides of iron are removed as a slag. For this purpose raw copper ore free from sulphur but containing much silica, and fluorspar to serve as a flux, are added to the calcined ore from (i), and the mixture is heated strongly with METAL-SLAG, a

silicate of iron containing small quantities of copper, obtained from operation (iii) below. In the melting operation the iron oxides combine with silica to form a fusible slag of iron silicate, ORE FURNACE SLAG, which contains only about 0·5 per cent. of copper; this floats and runs away, and at the end of the operation the lower layer of cuprous sulphide is run off through a tap hole in the bottom of the furnace into an iron box containing water to granulate it. The product known as COARSE METAL consists of a crude cuprous sulphide, Cu_2S, containing 30 to 34 per cent. of copper, 23 per cent. of sulphur, and considerable quantities of iron, arsenic, etc.

(iii) *Second Fusion.*—The coarse metal is again calcined and the product is treated once more as in (ii), by further fusion with raw oxide ore, and slags obtained in the later stages of purification, namely, ROASTER SLAG from (iv) and REFINERY SLAG from (v). This operation gives a much purer cuprous sulphide containing 70 to 80 per cent. of copper and 15 to 20 per cent. of sulphur, known as FINE METAL, and a slag, METAL SLAG, which is utilised in (ii) above.

(iv) *Roasting for Metal.*—The next process is that of roasting in a reverberatory furnace to obtain metallic copper. This is so arranged as to allow of partial oxidation in the first period, when half of the cuprous sulphide is oxidised to cupric oxide,

$$Cu_2S + 2O_2 = 2CuO + SO_2.$$

The air is then shut off and the temperature increased, when metallic copper is set free by the action shown in the following equation:

$$Cu_2S + 2CuO = 4Cu + SO_2.$$

The metal separates as a liquid together with a little ROASTER SLAG rich in copper, which is returned to the process at (iii). The copper is run off into sand moulds, where it solidifies; as it solidifies some sulphur dioxide escapes, which gives the metal the blistered appearance referred to in the name, BLISTER COPPER, which is applied to it. The crude metal still contains 2 to 3 per cent. of impurities (principally arsenic, 0·8 per cent.), and therefore has to be refined.

(v) *Refining.*—Blister copper in charges of 8 to 10 tons is melted in a stream of air. Any sulphur left is oxidised to sulphur dioxide, arsenic volatilises as As_4O_6, whilst iron, tin, and lead are converted into their oxides, which separate together with some copper oxide as a REFINERY SLAG which is returned to the process at (iii).

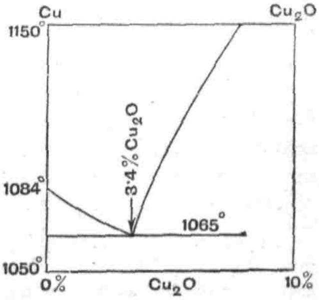


FIG. 277.—FREEZING-POINT DIAGRAM FOR COPPER AND CUPROUS OXIDE.

The purified metal, from which the slag has been separated by skimming, contains cuprous oxide (Fig. 277), which renders the metal brittle; to remedy this, powdered anthracite is sprinkled on the surface and the whole mass is stirred with a heavy pole of green birch wood. In this process, which is known as POLING, reducing gases are evolved which convert the oxide to metal and also serve to mix the metal thoroughly and to ensure uniformity of reduction. When correctly "poled," as judged by the quality of test pieces

Alloys of Copper.

(*a*) *Mechanical Properties of Pure Copper.*—Pure copper is a soft, tough metal, the mechanical properties of which resemble those of aluminium. Its toughness makes it an ideal material for withstanding shock, and undergoing deformation without cracking, provided that extreme strength is not also required ; it is therefore used extensively for steam-pipes which are exposed to much "hammering" by condensed water ; but even copper is liable to become hard and brittle if strained beyond the elastic limit, *e.g.*, when under hydraulic test. The tensile strength of copper, about 9 tons per square inch, is nearly twice as great as that of aluminium, but for equal weights aluminium is nearly twice as strong.* In the same way, although the electrical conductivity of aluminium is only 61 per cent. of that of an equal volume of copper, its conductivity is nearly twice as great when equal weights of the two metals are taken ; whilst, therefore, copper is almost always used for insulated wires and cables, as well as for the windings of electrical machinery, aluminium is a practicable alternative for conductors, such as overhead power-lines, which are not covered with an insulating material, and has been used occasionally for this purpose when the relative costs of the two metals make it economical to do so.

(*b*) *Solid Solutions.*—Copper differs from aluminium in the greater readiness with which it will blend with other metals to form both homogeneous liquid alloys and solid solutions. Thus it forms solid solutions in all proportions with nickel (Fig. 273), which immediately precedes it in the periodic classification of the elements, as well as with palladium, platinum, gold (Fig. 276), and manganese (Fig. 256) ; in the case of gold and of manganese, the freezing-point curve for the solid solutions passes through a minimum. The solid solutions of copper and *nickel*, including GERMAN SILVER, CONSTANTAN, etc., have already been described under Nickel (p. 805). The alloys of copper and *zinc*, including the commercial brasses, and the alloys of copper and *tin*, including the commercial bronzes, contain several series of solid solutions, each extending over a limited range of compositions, as described under (*e*) and (*f*) below.

(*c*) *Metallic and Quasi-metallic Compounds.*—Copper forms brittle compounds with many of the non-metals, as well as with some of the metals, *e.g.* :

Compound.	*Melting-point.*	*Compound.*	*Melting-point.*
Cu_3P (Fig. 71)	1025°	Cu_2O (Fig. 277)	
Cu_3As	830°	Cu_2S	1135°
Cu_3Sb	680°	$CuMg_2$	570°
Cu_3Si	862°	Cu_2Mg	797°

* In each case the tensile strength can be approximately doubled by rolling the cast metal into sheets, and in the case of copper the strength can be increased threefold by drawing into wire.

The compounds shown in this list all dissolve in molten copper and form eutectic alloys with it. These eutectics, crystallising out after the principal crystallisation of copper, make the metal brittle and lower its electrical conductivity to a remarkable degree. For this reason the complete purification of copper from oxygen, as well as from sulphur, arsenic, and metallic impurities, is of exceptional importance.

(*d*) *Eutectic Alloys.*—Copper forms an eutectic alloy with silver, the metal which immediately follows it in the group of coinage-metals, solid solutions being formed only up to 6 per cent. of copper in silver or 1 per cent. of silver in copper (Fig. 276, p. 825).

(*e*) *Brass.*—Copper and zinc unite to form a compound, Cu_2Zn_3, containing about 40 per cent. of copper, 60 per cent. of zinc; this is white like zinc, and all alloys containing more than 60 per cent. of zinc are classed as WHITE METAL. Alloys containing less than 60 per cent. of zinc consist of solid solutions of two types, as shown in Fig. 278, thus:

(i) Alloys containing up to 36 per cent. of zinc deposit solid solutions of the α-series, containing 0 to 30 per cent. of zinc, and isomorphous with copper; any excess of zinc above 30 per cent. is deposited as solid solution of the β-series, but can be reabsorbed by annealing (see below).

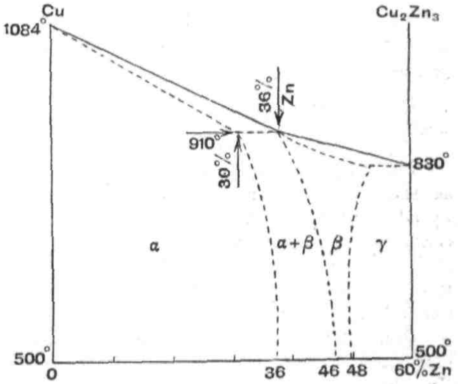


FIG. 278.—EQUILIBRIUM-DIAGRAM FOR BRASS.

(ii) Alloys containing from 36 to 60 per cent. of zinc deposit solid solutions of the β-series, containing 36 to 55 per cent. of zinc and perhaps isomorphous with the compound Cu_2Zn_3.

The range of the α-series can be extended to 36 per cent. of zinc by annealing at lower temperatures. On the other hand the range of the β-series is contracted from 36–55 per cent. to 46–48 per cent. of zinc at lower temperatures, any excess of zinc above 48 per cent. separating in the γ-form as the compound Cu_2Zn_3.

One of the most important of the commercial brasses is 70 : 30 brass, or CARTRIDGE BRASS. This represents the extreme limit of solubility of zinc in copper, to form solid solutions of the α-series at the temperature of solidification. Unlike copper, it becomes too brittle to be rolled readily when hot, but at atmospheric temperatures it is stronger and only slightly less plastic than copper; it has therefore a maximum capacity for withstanding deformation (*e.g.*, by pressing

and drawing in the cold) without cracking. An 80 : 20 alloy, with a golden-yellow colour, was formerly used as DUTCH METAL for cheap jewelry.

A second important alloy, 60 : 40 brass, or MUNTZ METAL, crystallises in the β-series and has the valuable property of being plastic when hot as well as in the cold. In the absence of tin, and all other hardening metals, it can be extruded through a die when red-hot, but when used for this purpose about 1 per cent. of the zinc is usually replaced by lead; this is so poor a solvent for copper that the eutectic alloy of the two metals is almost pure lead which may perhaps act as a lubricant during extrusion. This alloy is much harder than 70 : 30 brass, partly because β-brass is harder than α-brass, but perhaps also because the β-brass which it contains tends to deposit some α-brass during cooling (compare the hardening of iron by carbon, pp. 772 and 775). Its resistance to corrosion has also led to its use in sheathing ships. CAST BRASS is similar in composition to the brass used in extrusion, since it usually contains a small proportion of lead, but it need not be so pure, since the hardening effect of antimony, bismuth, tin, or silver is not important; the alloy may contain up to 75 per cent. of copper, but a proportion of 2 parts of copper to 1 part of zinc is very commonly used.

The alloy commonly known as MANGANESE BRONZE, or less inaccurately as MANGANESE BRASS, is usually a 60 : 40 brass or Muntz metal, deoxidised by adding a little manganese to the casting, and often including about 1 per cent. each of tin and iron; it has a tensile strength of about 30 tons per square inch with an elongation of about 20 per cent.; it is therefore as strong as mild steel and rather tougher, in addition to being much more resistant to corrosion.

DELTA METAL is a similar alloy deoxidised with copper phosphide, and containing a little lead to give increased resistance to corrosion (*e.g.*, Cu 55, Zn 43·5, Fe 1, Pb 0·4, P 0·1); it has a high tensile strength, is harder than copper, and can be forged and rolled; it is used for ships' propellers, where toughness and resistance to corrosion are specially important.

(*f*) *Bronze.*—The alloys of copper and tin show many points of analogy to those of copper and zinc; thus, two principal series of solid solutions, α and β, are formed by copper and tin, in addition to a colourless brittle compound, Cu_3Sn, containing $61\frac{2}{3}$ per cent. of copper; this limits the proportion of tin that can be usefully added to copper, just as the proportion of zinc is limited by the compound Cu_2Zn_3. Again, alloys containing up to 25 per cent. of tin deposit solid solutions of the α-series, containing up to 9 per cent. of tin, this range being increased to about 13 per cent. by annealing at lower temperatures. Alloys containing more than 25 per cent. of tin deposit solid solutions of the β-series, which are more brittle than those of the α-series, since the compound Cu_3Sn readily crystallises out from them; these

β-crystals are also the form in which the excess of tin above 9 per cent. is deposited from alloys containing under 25 per cent. of tin. In all the commercial bronzes the proportion of tin is under 25 per cent. and the first crystals to separate belong to the α-series of solid solutions; but SPECULUM METAL, a white metal which can be used for making mirrors, since it takes a high polish and does not tarnish, contains about 33 per cent. of tin and crystallises in the β-series.

COINAGE BRONZE contains 4 per cent. of tin and 1 per cent. of zinc. SOFT BRONZE, or GUN-METAL, for instruments, gear wheels, etc., contains from 8 to 12 per cent. of tin, the strength of the alloy increasing and its ductility diminishing slightly as the proportion of tin increases. HARD BRONZE, or BELL-METAL, owes its greater hardness to the separation of solid solutions of the β-series, in addition to the α-crystals which are the primary separation; these alloys may contain from 12 to 24 per cent. of tin, but never contain enough tin to give a primary separation of β-crystals.

PHOSPHOR-BRONZE (*e.g.*, Cu 82, Sn 12·5, Pb 4, P 1·5 per cent.) varies very widely in composition, but is in general a gun-metal deoxidised with phosphorus (added as phosphor-copper, p. 184, or phosphor-tin), and often containing lead to give increased resistance to corrosion and to reduce friction (compare Delta metal). It is one of the strongest of the non-ferrous metals and is used extensively as a substitute for steel where rusting and corrosion must be avoided, *e.g.*, for machine-parts, bearings, pump-linings, valves, taps, etc.

Chemical Properties of Copper.

(*a*) *Classification.*—The most remarkable feature of the chemistry of copper is its divergence, not only from the metals of the alkalies, but even from the other two metals of the coinage-group, and its close adhesion to the series of transition-elements of which it is also a member. Thus metallic copper is isomorphous with nickel, which precedes it, and forms two series of solid solutions with zinc, which follows it in the transition series, but it gives an eutectic alloy with silver, its immediate homologue in the family of coinage metals, and a drooping freezing-point curve when alloyed with gold. The compounds of copper show a still more striking contrast, since almost all the most important salts are bivalent compounds which have no analogy amongst the salts of silver and gold; they are, however, similar to and in many cases isomorphous with the corresponding salts of nickel and zinc. Even the univalent salts of copper resemble those of mercury, in the next column, rather than the univalent salts of its homologues silver and gold.

(*b*) *Valency.*—The principal compounds of copper may be classed under two headings as CUPROUS and CUPRIC COMPOUNDS, derived from the oxides Cu_2O and CuO respectively.

	Oxides.	Chlorides.	Bromides.	Iodide.
Cuprous Compounds .	Cu_2O	Cu_2Cl_2	Cu_2Br_2	Cu_2I_2
Cupric Compounds .	CuO	$CuCl_2$	$CuBr_2$	—
	Cyanide.	*Sulphides.*	*Sulphate.*	*Nitrate.*
Cuprous Compounds .	$Cu_2(CN)_2$	Cu_2S	—	—
Cupric Compounds .	—	CuS	$CuSO_4$	$Cu(NO_3)_2$

Cuprous nitrate is not known, and cuprous sulphate is only known with certainty in its derivatives. In the same way cupric iodide and cupric cyanide are too unstable to be isolated, although derivatives of both salts have been prepared. The cuprous salts as a class are colourless and insoluble in water; the cupric salts are easily soluble in water and give blue solutions.

In the cupric compounds, copper is certainly bivalent; in the cuprous compounds, the valency is probably the same, since the vapour density of cuprous chloride shows it to have the formula Cu_2Cl_2, that is Cl.Cu.Cu.Cl, and not CuCl, even at quite high temperatures. The molecular weight of cuprous cyanide as determined from the depression of the freezing-point of certain organic solvents also corresponds with the double formula $Cu_2C_2N_2$.

(*c*) *Combination with Non-metals.*—Copper combines directly with oxygen to form **cupric oxide,** CuO, but if the temperature is high **cuprous oxide,** Cu_2O, is formed, *e.g.*, molten copper gives only cuprous oxide. Copper also combines directly with sulphur, with chlorine, and with phosphorus. It does not form a hydride by direct combination with hydrogen, although a **cuprous hydride,** Cu_2H_2, is said to be formed as a brown precipitate by reducing aqueous copper sulphate with hypophosphorous acid, and to yield a **cupric hydride,** CuH_2, when heated. The fact that copper, like nickel, is an excellent catalyst for the addition or removal of hydrogen in organic chemistry, *e.g.*,

$$\underset{\text{Alcohol}}{C_2H_6O} \rightleftharpoons \underset{\text{Aldehyde}}{C_2H_4O} + H_2,$$

suggests, however, that some compound such as CuH_2 may be formed as an active intermediate product in these actions.

(*d*) *Action of Air and Water.*—Copper is not affected by exposure to pure dry air, but in ordinary moist air it becomes covered with VERDIGRIS, consisting mainly of the basic carbonate, $CuCO_3,Cu(OH)_2$.

Pure distilled water free from carbon dioxide and salts has no action on copper. Distilled water, prepared in copper stills, however, invariably contains traces of copper, probably owing to the action of traces of ammonia on the metal in presence of oxygen; its presence can be shown, even when it cannot be detected readily by chemical methods, by its toxic effect on the growth of plants. Water containing dissolved salts rapidly corrodes copper, ammonium salts being especially active in this respect. Sea-water also rapidly attacks copper, which is therefore not the most suitable metal for sheathing ships. Brass is less attacked, but special alloys such as Muntz metal and Delta metal are generally used for sheathing as well as for ships' propellers

(e) *Action of Acids.*—In the absence of air, dilute sulphuric acid does not act on copper even when boiling, but in presence of air the copper dissolves gradually, forming a solution of the sulphate,

$$2Cu + O_2 + 2H_2SO_4 = 2CuSO_4 + 2H_2O$$

Copper is also dissolved by concentrated sulphuric acid, liberating sulphur dioxide from it,

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O;$$

cuprous sulphide and free sulphur are, however, also formed as secondary products of this action.

Cold hydrochloric acid is without action on copper in the absence of air; but finely divided copper, when heated with the concentrated acid, slowly liberates hydrogen and forms cuprous chloride:

$$2Cu + 2HCl = Cu_2Cl_2 + H_2.$$

When free from nitrous acid, dilute nitric acid of density 1·07 to 1·2 does not attack copper, but on adding a trace of a nitrite, action begins at once and continues vigorously until the metal is dissolved. Ordinary dilute nitric acid attacks copper rapidly even when cold; the principal gaseous product is nitric oxide, the formation of which can be represented by the equation

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O;$$

but other oxides, such as nitrous oxide, are formed in proportions which vary with the concentration of acid, temperature, etc.

(f) *Co-ordinated Compounds.*—It has already been shown that the power of forming stable co-ordinated compounds is at a maximum in cobalt and is much diminished in nickel. In the case of copper, a few of these compounds appear to be formed, but they are so unstable that the co-ordinated groups can usually be detected by the common tests, and in many cases they are decomposed merely by dilution or by exposure to air either at atmospheric temperatures or on heating. Some of these compounds in which co-ordination may be suspected are:

(i) *Cuprous Compounds*—

$Cu_2Cl_2,2HCl$ or $H_2Cu_2Cl_4$; compare H_2PtCl_4 or $H_2[Pt.4Cl]$
$Cu_2Cl_2,2NH_3$; compare $PtCl_2,2NH_3$ or $[Pt.2NH_3.2Cl]$
$4NH_4Cl,Cu_2Cl_2$ or $(NH_4)_4Cu_2Cl_6$; compare K_2PtCl_6 or $K_2[Pt.6Cl]$.

(ii) *Cupric Compounds*—

$CuCl_2,2HCl,5H_2O$ or $H_2CuCl_4,5H_2O$; compare H_2PtCl_4 or $H_2[Pt.4Cl]$
$CuC_2N_2,2KCN$ or $K_2CuC_4N_4$; compare $K_2PtC_4N_4$ or $K_2[Pt.4CN]$
$CuCl_2,6NH_3$ and $CuCl_2,4NH_3$; compare $PtCl_2,4NH_3$ or $[Pt.4NH_3]Cl_2$
$CuSO_4,4NH_3$ and $Cu(OH)_2,4NH_3$;
compare $Pt(OH)_2,4NH_3$ or $[Pt.4NH_3](OH)_2$
$K_2CaCu(NO_2)_6,6H_2O$ or $K_2Ca[Cu.6NO_2],6H_2O$;
compare $K_3[Co.6NO_2]$ and $K_2[Pt.4NO_2.2Cl]$

Cuprous Compounds.

Cuprous Chloride, Iodide, and Cyanide.

Cuprous chloride, Cu_2Cl_2, is prepared by heating a solution of cupric oxide in hydrochloric acid with copper turnings,

$$CuO + Cu + 2HCl = Cu_2Cl_2 + H_2O.$$

On pouring the solution into a large volume of water a white precipitate of cuprous chloride separates.

It can also be prepared by passing sulphur dioxide through a solution of copper sulphate to which common salt has been added in equivalent proportions,

$$2CuSO_4 + 4NaCl + 2H_2O + SO_2 = Cu_2Cl_2 + 2HCl + 2Na_2SO_4 + H_2SO_4;$$

as the sulphur dioxide is passed through the solution, cuprous chloride separates as a white crystalline precipitate.

Cuprous chloride crystallises in white tetrahedra, but is gradually oxidised by air, turning yellow or green; the final product is the basic cupric chloride, $3CuO,CuCl_2,3H_2O$, described below (p. 841). It is sparingly soluble in water, but dissolves readily in concentrated hydrochloric acid, giving a dark brown solution from which the compound $Cu_2Cl_2,2HCl$ has been separated. It also dissolves in concentrated ammonia, forming, when air is excluded, a colourless solution from which the colourless salt $Cu_2Cl_2,2NH_3$ has been separated; but, when allowed to oxidise, it gives a blue solution from which violet crystals of the composition $CuCl_2,Cu_2Cl_2,4NH_3,2H_2O$ have been separated.

Both acid and ammoniacal solutions are employed for the absorption of carbon monoxide in gas analysis; on continued passage of this gas the compound $Cu_2Cl_2,CO,2H_2O$ separates in colourless crystals; from solid cuprous chloride the compound $Cu_2Cl_2,2CO,4H_2O$ has been prepared (compare $PtCl_2,CO$ and $PtCl_2,2CO$, p. 816). On passing acetylene through a solution of cuprous chloride in ammonia, red **cuprous acetylide,** Cu_2C_2,H_2O, is precipitated.

Cuprous iodide, Cu_2I_2, is precipitated on adding potassium iodide to a solution of cupric sulphate, since cupric iodide is unstable and decomposes into iodine and cuprous iodide,

$$2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4.$$

This action is made use of in the volumetric estimation of copper, the iodine set free being titrated with sodium thiosulphate.

Cuprous cyanide, $Cu_2C_2N_2$, is formed, in just the same way as cuprous iodide, as an insoluble white precipitate on adding potassium cyanide to a solution of copper sulphate,

$$2CuSO_4 + 4KCN = Cu_2C_2N_2 + C_2N_2 + 2K_2SO_4;$$

the cyanogen set free in this action is, however, contaminated with hydrogen cyanide. Cuprous cyanide dissolves in an excess of potass-

ium cyanide, forming the colourless compound $KCuC_2N_2$, compare $KAgC_2N_2$ and $KAuC_2N_2$.

Cuprous Oxide, Sulphide, and Sulphate.

Cuprous oxide, Cu_2O, occurs as CUPRITE, or red copper ore, and as a beautiful hair-like mass in CHALCOTRICHITE. It is most readily prepared by reducing an alkaline solution of copper tartrate (FEHLING'S SOLUTION) with a reducing sugar (invert-sugar or dextrose); on warming, cuprous oxide separates as a brilliant red powder. This reduction to cuprous oxide is used in the estimation of sugars, either gravimetrically (the cuprous oxide being oxidised to cupric oxide or reduced to metallic copper before weighing it) or volumetrically, the blue colour of the cupric solution rendering the use of an indicator unnecessary. With dilute sulphuric acid cuprous oxide forms cupric sulphate, copper being liberated,

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O.$$

Cuprous sulphide, Cu_2S, is the principal source of copper. It occurs as CHALCOCITE or COPPER GLANCE, and in combination with ferric sulphide as COPPER PYRITES, $CuFeS_2$. It is formed on burning copper in sulphur vapour or by reducing cupric sulphide, CuS, in a current of hydrogen.

Cuprous sulphate, Cu_2SO_4, can be prepared in solution by the action of metallic copper on aqueous solutions of cupric sulphate, which will dissolve appreciable quantities of the metal; the solutions, which deposit copper on cooling, give an electrochemical equivalent slightly higher than that of cupric copper, and evidently contain a small proportion of the cuprous salt. By saturating the liquid with carbon monoxide a colourless solution is obtained from which crystals of the **carbonyl**, $Cu_2SO_4,2CO,H_2O$, can be separated. When dissolved in ammonia, this loses its carbon monoxide in a vacuum, and gives the colourless **tetrammine**, $Cu_2SO_4,4NH_3$, which has been prepared in colourless crystals by reduction of an ammoniacal cupric solution with hydroxylamine sulphate.

CUPRIC COMPOUNDS.

Cupric Chloride, Bromide, Iodide, and Cyanide.

Cupric chloride, $CuCl_2$, is formed by burning copper in chlorine, or by careful dehydration of the hydrated salt. The anhydrous salt is yellowish-brown in colour; it melts at about 500°, and is thereby converted into cuprous chloride and chlorine,

$$2CuCl_2 = Cu_2Cl_2 + Cl_2.$$

It is deliquescent and very soluble in water, giving a green solution which when very dilute becomes blue; from the solution green crystals

of the **dihydrate,** $CuCl_2,2H_2O$, can be obtained. This hydrate can be prepared by dissolving copper oxide or carbonate in hydrochloric acid and evaporating the solution.

Well-crystallised double salts, such as $CuCl_2,KCl$ or $KCuCl_3$, and $CuCl_2,2KCl,2H_2O$ or $K_2CuCl_4,2H_2O$, crystallising in blue plates, are formed by combination with potassium chloride; similar compounds can be obtained with ammonium chloride. On cooling to $-16°$, a solution of cupric chloride saturated with hydrogen chloride deposits red crystals of $CuCl_2,2HCl,5H_2O$, which lose their acid and leave a residue of the dihydrate, $CuCl_2,2H_2O$, on exposure to air; by somewhat similar methods the compound $CuCl_2,HCl,2H_2O$ has been prepared. These two compounds may be regarded as hydrates of the acids, $HCuCl_3$ and H_2CuCl_4, from which the double salts are derived; they are, however, much less stable than the acids formed by auric and platinic chlorides, $HAuCl_4$ and H_2PtCl_6.

Compounds of cupric chloride with ammonia of the formulæ $CuCl_2,2NH_3$, $CuCl_2,4NH_3$, and $CuCl_2,6NH_3$ have been described (compare $ZnCl_2$). These are perhaps co-ordinated compounds (p. 797), but they are readily decomposed, *e.g.*, the hexammine loses $2NH_3$ at 90°, and the tetrammine at 135°, whilst the diammine is decomposed completely at 180° to 300°, liberating ammonia, ammonium chloride, and nitrogen, and leaving a residue of cuprous chloride.

Cupric bromide, $CuBr_2$, crystallises from water in green needles of the composition $CuBr_2,4H_2O$.

Cupric iodide is not known, but the **tetrammine,** $CuI_2,4NH_3,H_2O$, is obtained as a blue crystalline precipitate by adding an excess of potassium iodide to a saturated ammoniacal solution of copper sulphate or copper acetate.

Cupric cyanide is not known, but the double cyanide, $K_2CuC_4N_4$, compare $K_2ZnC_4N_4$, $K_2PdC_4N_4$, and $K_2PtC_4N_4$, can be separated in colourless crystals from the solutions prepared by adding an excess of potassium cyanide to cupric sulphate.

Cupric Oxide and Hydroxide.

Cupric oxide, or **black oxide of copper,** CuO, occurs as BLACK COPPER ORE. It can be prepared by heating cupric hydroxide, cupric carbonate, or cupric nitrate, or by burning copper in air or oxygen at moderate temperatures, but if heated strongly it dissociates into cuprous oxide and oxygen,

$$4CuO \rightleftharpoons 2Cu_2O + O_2.$$

In a vacuum, this dissociation begins at about 350°; the oxide therefore parts with oxygen very readily, and is commonly used to oxidise organic compounds in the combustion furnace, when the oxide is reduced to metal, whilst the organic compound is burnt to water and carbon dioxide. Copper oxide prepared by burning thin copper wire is par-

ticularly suitable for use in analysis by combustion (p. 102). Cupric oxide dissolves readily in dilute acids, forming cupric salts.

Cupric hydroxide, $Cu(OH)_2$, is obtained as a light blue precipitate by adding sodium hydroxide to a cold solution of a cupric salt; if warmed during precipitation, the hydroxide loses water and a black substance, having the composition $Cu(OH)_2,3CuO$, is obtained, which Sabatier regards as

$$HO{\cdot}Cu{\cdot}O{\cdot}Cu{\cdot}O{\cdot}Cu{\cdot}O{\cdot}Cu{\cdot}OH\text{ ; compare } NaO{\cdot}SiO{\cdot}O{\cdot}SiO{\cdot}O{\cdot}SiO{\cdot}O{\cdot}AlO.$$

It is the parent substance of a series of crystalline BASIC SALTS, which are obtained by leaving the black hydroxide in contact with solutions of the normal salts, *e.g.*,

Basic copper chloride, $3CuO,CuCl_2,3H_2O$ (occurs as a mineral and is prepared artificially as Brunswick green by the action of hydrochloric acid on copper exposed to air).
Basic copper bromide, $3CuO,CuBr_2,3H_2O$.
Basic copper nitrate, $3CuO,Cu(NO_3)_2,3H_2O$ (see below, p. 843).
Basic copper sulphate, $3CuO,CuSO_4,4H_2O$ (occurs as a mineral, pp. 827 and 843).

Cupric hydroxide dissolves in ammonia, forming a dark blue solution which probably contains **cuprammonium hydroxide,** $[Cu.4NH_3](OH)_2$; this compound is, however, unstable and deposits cupric hydroxide when diluted with much water. The ammoniacal solution dissolves cellulose (filter-paper, cotton wool) and has been used in waterproofing canvas (Willesden goods) and in the manufacture of artificial silk (Pauly process).

Copper Carbonates.

(*a*) *Double Carbonates.*—Normal cupric carbonate, $CuCO_3$, is not known, although well-defined crystalline DOUBLE CARBONATES, such as $CuCO_3,Na_2CO_3$ or $Cu(CO_3Na)_2$, and $CuCO_3,K_2CO_3$ or $Cu(CO_3K)_2$, have been prepared with and without water of crystallisation (compare potassium magnesium carbonate, $Mg(CO_3K)_2$, etc., p. 619). Thus when a concentrated solution of potassium carbonate is added to a concentrated solution of copper sulphate, the blue precipitate which is first formed consists largely of **potassium cupric carbonate,** $Cu(CO_3K)_2$, or a hydrate thereof. The principal action is, therefore, not (as in the case of calcium)

$$CuSO_4 + K_2CO_3 = CuCO_3 + K_2SO_4,$$

but

$$CuSO_4 + 2K_2CO_3 = Cu(CO_3K)_2 + K_2SO_4.$$

(*b*) *Basic Carbonates.*—On adding water to the double carbonate and stirring, the colour of the precipitate changes from blue to green,

and under suitable conditions a basic carbonate approximating in composition to MALACHITE, $CuCO_3,Cu(OH)_2$, is obtained.

$$2Cu(CO_3K)_2 + 2H_2O = CuCO_3,Cu(OH)_2 + K_2CO_3 + 2KHCO_3.$$

The structure of this is probably $CO(\cdot O\cdot Cu\cdot OH)_2$. If a concentrated solution of potassium carbonate be added to the green basic carbonate, the precipitate dissolves again, giving a solution of the blue potassium copper carbonate from which crystals of the salt, $Cu(CO_3K)_2$ (dark blue crystalline powder), or the monohydrate, $Cu(CO_3K)_2,H_2O$ (blue silky needles), or the tetrahydrate, $Cu(CO_3K)_2,4H_2O$ (greenish-blue plates), separate according to the concentration of the liquid.

It is probable that (as in the case of the basic carbonates of magnesium, p. 618) most of the basic carbonates of copper which have been described are mixtures. Two crystalline and well-defined basic carbonates of copper are, however, found in nature as the minerals MALACHITE, $CuCO_3,Cu(OH)_2$, which occurs in prisms or in fibrous silky masses of an emerald green colour, and AZURITE or CHESSYLITE, $2CuCO_3,Cu(OH)_2$, which forms magnificent blue crystals. These readily lose carbon dioxide when heated either alone at a temperature slightly above 200° or with boiling water, and give the brownish-black **base,** formulated above as $3CuO,Cu(OH)_2$; at higher temperatures the black oxide, CuO, is formed.

Cupric Sulphide and Sulphate.

Cupric sulphide, CuS, occurs in the massive state as INDIGO COPPER or COVELLITE. It is formed on precipitating a solution of a cupric salt with hydrogen sulphide as a black precipitate, which is insoluble in dilute acids but soluble in nitric acid.

Cupric sulphate, $CuSO_4,5H_2O$, or BLUE VITRIOL, is the most widely used copper salt. It is obtained by the action of hot dilute sulphuric acid on copper (or on minerals containing copper) in contact with air.

$$2Cu + O_2 + 2H_2SO_4 = 2CuSO_4 + 2H_2O.$$

In order to prepare it, copper scrap, granulated copper, or copper turnings are placed in a lead-lined tower down which dilute sulphuric acid is sprayed, whilst a current of air is pumped in at the base so as to meet the descending stream of acid. The copper dissolves, and the solution is circulated until a sufficient concentration of copper sulphate is reached. The action generates heat which facilitates the solution of the metal. Alternatively, the scrap copper may be heated to oxidise it to copper oxide before treatment with acid. Large quantities of copper sulphate are also made by the extraction of cupriferous pyrites which has been burnt for the preparation of sulphur dioxide in th manufacture of sulphuric acid.

Copper sulphate crystallises from water in deep blue prisms of th **pentahydrate,** $CuSO_4,5H_2O$ (Fig. 37, p. 47), belonging to the asym

metric system (Fig. 91, p. 213). These dissolve in three times their weight of water at 0° and in half their weight of water at 100°. When the pentahydrate is heated at 100° it loses $4H_2O$ and gives the **monohydrate,** $CuSO_4,H_2O$. The final molecule of water is expelled between 220° and 260°, although a little water (0·04 per cent.) is retained even at 360°. The anhydrous salt is white, extremely hygroscopic, and can be used for dehydrating various liquids.

The stability of the monohydrate may be explained by regarding it as a compound of the formula $HO·Cu·O·SO_2·OH$. This view is supported by the fact that anhydrous copper sulphate absorbs hydrogen chloride gas, giving a compound, $Cl·Cu·O·SO_2·OH$, which on treatment with water gives sulphuric acid and cupric chloride. Solutions of copper sulphate have a distinct acid reaction; this may be attributed to the weak basicity of cupric hydroxide, or to the natural acidity of a compound of the formula $HO·Cu·O·SO_2·OH$.

Copper sulphate is used in copper-plating, in dyeing and calico printing, and for preserving wood and hides. It is used in agriculture, for spraying potatoes, vines, etc., in order to destroy insect and fungoid pests; for this purpose it is frequently mixed with lime, as BORDEAUX MIXTURE, or with sodium carbonate, as BURGUNDY MIXTURE. The active constituent of Bordeaux mixture is probably the basic sulphate, $3CuO,CuSO_4$, aq. (p. 841); Burgundy mixture is more complex and may contain both basic carbonates and basic sulphates.

Numerous BASIC SULPHATES have been described of which two, having the compositions $3CuO,CuSO_4,3H_2O$ or $3Cu(OH)_2,CuSO_4$ and $3CuO,CuSO_4,4H_2O$, or $3Cu(OH)_2,CuSO_4,H_2O$, are found as minerals.

Cupric Nitrate, $Cu(NO_3)_2,3H_2O$.

This salt is obtained by dissolving copper or its oxide or carbonate in dilute nitric acid, and crystallising the solution; it forms bright blue crystals, which are very soluble in water and are deliquescent. The anhydrous nitrate is not known, as on heating it loses nitric acid and forms the **basic salt,** $3Cu(OH)_2,Cu(NO_3)_2$ (p. 841). The **tetrammine,** $Cu(NO_3)_2,4NH_3$, forms blue prisms, and is very violently explosive.

Detection and Estimation of Copper.

Volatile copper salts such as the chloride and nitrate impart a green colour to the Bunsen flame, and the same behaviour is shown by other compounds of copper when mixed with a chloride or moistened with hydrochloric acid. Copper salts are reduced to red metallic copper when heated with charcoal or on a charcoal block in a reducing flame.

Copper salts are precipitated by hydrogen sulphide from acid solutions, as **cupric sulphide,** CuS, a black compound which is insoluble in potassium hydroxide, in ammonium sulphide, and in boiling dilute sulphuric acid, but which dissolves in boiling nitric acid or potassium

cyanide. When a copper salt is treated with ammonia a pale blue precipitate is formed which immediately redissolves, forming a dark blue solution. With potassium ferrocyanide cupric salts give a reddish-brown coloration or precipitate of **cupric ferrocyanide,** $Cu_2FeC_6N_6$. On immersing a strip of iron in a solution of a copper salt it becomes covered with a layer of metallic copper.

Copper is usually estimated either as oxide, sulphide, or metal. For estimation as **oxide** the solution is precipitated with potassium or sodium hydroxide in hot dilute solution, washed by repeated decantation, and collected on a filter-paper or Gooch crucible, but this method is not satisfactory, as the precipitate carries down and retains some of the alkali. An alternative method of preparation is as **cuprous thiocyanate**, CuCNS, in presence of a reducing agent such as sulphur dioxide, the granular precipitate being collected and dried at 110° to 120°. The electrolytic method of separation as metal is rapid, accurate, and widely used. A volumetric method of estimation, based on the liberation of iodine from potassium iodide by a copper salt and subsequent titration with sodium thiosulphate, is also rapid and accurate; copper ores are, however, usually valued by titrating the copper in a deep-blue ammoniacal solution against potassium cyanide, which decolorises it.

The atomic weight of copper is based on exact determinations of the electrochemical equivalents of the metals Cu and Ag, and on determinations of the ratios CuO : Cu and Cu : 2AgBr.

47. Silver. Ag = 107·88.

Occurrence.

(*a*) *Native silver* occurs in many localities, but especially in Canada, where very large quantities are obtained in the neighbourhood of the town of Cobalt in Ontario, from a vein of quartz heavily charged with metallic silver.

(*b*) Silver is also present in larger or smaller proportions as an isomorphous impurity in nearly all copper and lead ores; large quantities of silver are therefore obtained in the refining of lead and of copper as well as from the burnt pyrites of the sulphuric acid manufacturer.

(*c*) *Important ores of silver* are:

Silver sulphide, Ag_2S, (i) as SILVER GLANCE, or ARGENTITE, Ag_2S, a cubic mineral isomorphous with galena, PbS;

(ii) as SILVER COPPER GLANCE $[Cu,Ag]_2S$; that is, copper glance in which part of the copper is replaced by silver, the silver sulphide being here carried down in an orthorhombic form;

(iii) as PYRARGYRITE, or RUBY SILVER ORE, a **silver sulphantimonite** of the formula $3Ag_2S,Sb_2S_3$ or Ag_3SbS_3.

Silver chloride, AgCl, as CHLOROARGYRITE or HORN SILVER.

Preparation of Metallic Silver.

In separating metallic silver from its compounds, advantage is taken of the fact that silver oxide decomposes into metallic silver and oxygen when heated, whilst other metals such as lead and copper form stable oxides. Thus, it is the instability of the oxide and carbonate which makes it possible to recover metallic silver from silver chloride residues merely by heating them with sodium carbonate,

$$2AgCl + Na_2CO_3 = Ag_2CO_3 + 2NaCl$$
$$Ag_2CO_3 = Ag_2O + CO_2 = 2Ag + CO_2 + \tfrac{1}{2}O_2.$$

Another fact utilised in extracting silver is that the metal dissolves readily in other metals such as lead and mercury, and its sulphide mixes freely with other metallic sulphides; crude metallic lead therefore contains all the silver originally present in the ore, and the "fine metal" (Cu_2S) described on p. 829 contains the whole of the silver of the copper ore and, on reduction to metal, yields an argentiferous copper. The silver in the copper is recovered by electrolytic refining, whilst the silver in lead is recovered by concentration and cupellation as described below.

The silver present in silver ores as sulphide can be precipitated by mercury after conversion to chloride (amalgamation process, see below). Silver can also be extracted both from calcined silver ores and from argentiferous burnt pyrites by roasting with salt and extracting the silver chloride, in the former case with sodium thiosulphate, and in the latter case with a hot solution of common salt, in which silver chloride is appreciably soluble. The silver in the thiosulphate solution is precipitated as sulphide, regenerating the thiosulphate, and converted into metal by strong ignition.

$$AgCl + Na_2S_2O_3 = NaAgS_2O_3 + NaCl$$
$$Na_2S + 2NaAgS_2O_3 = 2Na_2S_2O_3 + Ag_2S$$
$$Ag_2S + O_2 = 2Ag + SO_2.$$

The silver in the brine is precipitated as iodide and reduced to metal by zinc and hydrochloric acid, regenerating zinc iodide for further use.

The MEXICAN PROCESS for extracting silver by amalgamation dates back to 1557, and is of special value in localities where fuel and water are scarce. The ore, containing silver sulphide, Ag_2S, and silver chloride, $AgCl$, with some free metal, is ground, mixed with 2 to 5 per cent. of common salt, and thoroughly incorporated by the treading of mules on a circular paved floor. After a day or two, mercury is added, and ½ to 2 per cent. of "magistral," that is, weathered copper pyrites containing copper sulphate and ferric sulphate; after an interval more mercury is added and again thoroughly incorporated by treading. Three lots of mercury are usually added at intervals of fifteen days, the mixture being worked from time to time. Under these conditions the silver is reduced to metal and forms an amalgam with the mercury. This is washed with water, squeezed through canvas bags, and distilled. The mercury is condensed and used again, whilst the crude silver which is

left is refined by cupellation. The changes occurring in this process may be formulated as follows:

$$CuSO_4 + 2NaCl = Na_2SO_4 + CuCl_2$$
$$2CuCl_2 + Ag_2S = Cu_2Cl_2 + 2AgCl + S$$
$$Cu_2Cl_2 + Ag_2S = Cu_2S + 2AgCl$$
$$2AgCl + 2Hg = Hg_2Cl_2 + 2Ag.$$

The process involves considerable loss of mercury, not only mechanically, but owing to the formation of calomel, which is lost. It is therefore being replaced by a cyanide process, similar to that used for the extraction of gold.

Extraction of Silver from Lead.

The crude lead, sometimes enriched by smelting with poor silver ores, contains all the silver and is usually concentrated by Pattinson's or Parkes's process (p. 691) until it contains 200 to 500 oz. per ton, or about 1 per cent. of silver, and is then cupelled.

The CUPELLATION is carried out in a CUPEL or porous hearth which is composed of a mixture of marl and bone-ash, or now more frequently of Portland cement, and supported in an iron framework (Fig. 279). The cupel is heated in a reverberatory furnace, arranged so that the flames from a

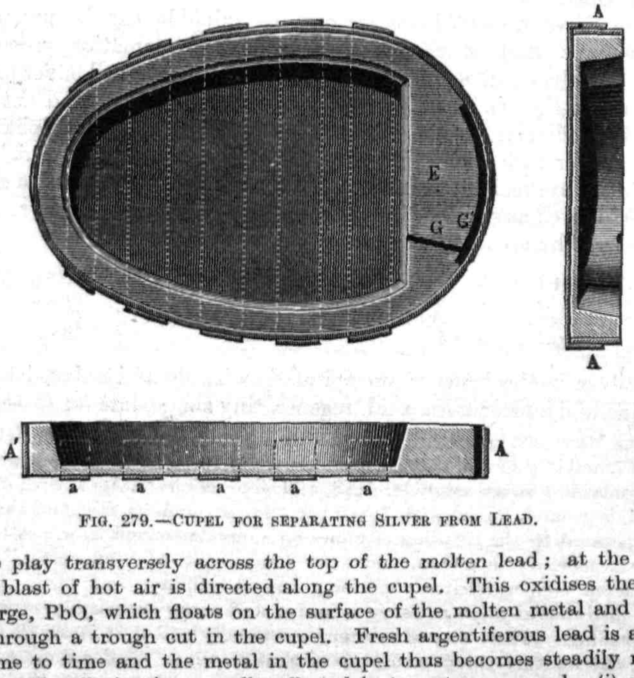


FIG. 279.—CUPEL FOR SEPARATING SILVER FROM LEAD.

coal-fire play transversely across the top of the molten lead; at the same time a blast of hot air is directed along the cupel. This oxidises the lead to litharge, PbO, which floats on the surface of the molten metal and flows away through a trough cut in the cupel. Fresh argentiferous lead is added from time to time and the metal in the cupel thus becomes steadily richer in silver. Cupellation is generally effected in two stages, namely, (i) a first cupellation, up to 60 to 70 per cent. of silver, giving a litharge which is practically free from silver; (ii) a second cupellation, in a cupel containing a larger

proportion of bone-ash, giving an argentiferous litharge which is re-worked for silver, and also leaving some silver in the cupel which can be extracted when the cupel is worn out and broken up.

After burning out the lead, the metal remaining in the cupel contains 99·7 to 99·8 per cent. of silver, but it can be further refined by cupellation at a higher temperature, when the last traces of copper, lead, and bismuth are oxidised and a FINE METAL containing 99·9 per cent. or more of pure silver is produced. The traces of gold which remain in the fine silver can be recovered by electrolysis, when the gold remains behind as an anode slime.

Physical Properties of Metallic Silver.

Silver is a white metal of density 10·5. It is very tough, malleable, and ductile (1 gram can be drawn out into a wire 1800 metres, or more than a mile, in length), and of all metals it is the best conductor of heat and electricity.

Silver melts at 960° and boils at 1955°; its vapour density corresponds with a molecular weight of 108, so that the metal is monatomic.

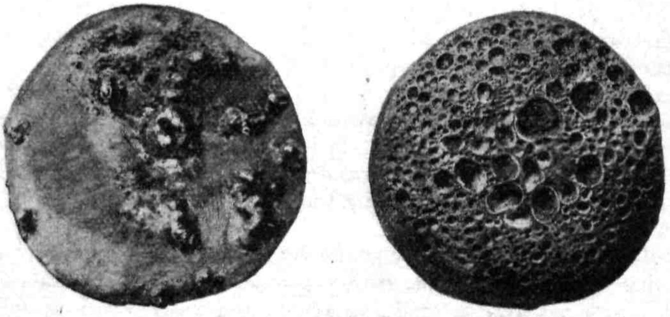


FIG. 280.—BUTTON OF SILVER SHOWING THE EFFECTS OF "SPITTING."

The molten metal absorbs more than twenty times its volume of oxygen, but this is expelled again when the metal cools, giving rise to the phenomenon of SPITTING (Fig. 280). It is well known that cuprous oxide, Cu_2O, dissolves in molten copper (Fig. 277), lowering its melting-point by nearly 20°; but since it is not isomorphous with solid copper, it separates from it on crystallisation, rendering the metal brittle and destroying its electrical conductivity. The spitting of silver probably depends on the dissolution of silver oxide, Ag_2O, in molten silver, and its decomposition into silver and oxygen when it is thrown out of solution by the crystallisation of the metal. This view is supported by the fact that the freezing-point of silver is lowered from 960° to 955° by the absorption of oxygen.

Alloys of Silver.

Silver is generally used as an alloy with copper; thus, COINAGE SILVER contained 92·5 per cent. of silver, 7·2 per cent. of copper, 0·2 per cent. of lead, and 0·1 per cent. of gold. The copper, of which about

6 per cent. can be taken up in solid solution in the silver, makes the metal hard, increases its strength and toughness, and at the same time lowers its melting-point. The fineness of silver is calculated on one thousand parts, so that coinage silver, for instance, was said to have a fineness of 925. The silver used in making articles of plate and jewelry may contain 75 to 85 per cent. of silver, but in this country standard silver, 925 fine, has been used almost exclusively, since poorer alloys were not legal, and richer alloys are not often made. The introduction of small quantities of cadmium, which forms a series of solid solutions with silver, renders the cast alloy free from blow-holes, whilst larger quantities make the product less liable to tarnish.

Chemical Properties of Silver.

Silver is a noble metal which does not oxidise in air, even when heated; the spitting of silver is, however, probably due to the decomposition of silver oxide, Ag_2O, dissolved in the molten metal. In the same way, it has been suggested that the slight disintegration of the surface which takes place when silver is heated in hydrogen may be due to the formation and decomposition of an unstable hydride.

Although not attacked by oxygen, silver tarnishes rapidly in an atmosphere containing sulphuretted hydrogen owing to the formation of black silver sulphide, Ag_2S. It is attacked by chlorine, bromine, and iodine, especially at temperatures above the melting-point of the product, but in the case of chlorine the action can be stopped by careful drying.

Silver is not attacked by dilute hydrochloric or sulphuric acid, but dissolves readily in hot, strong sulphuric acid and in dilute nitric acid, which act also as oxidising agents and are reduced to sulphur dioxide and to oxides of nitrogen, *e.g.*,

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O;$$

in the absence of lower oxides of nitrogen, however, dilute nitric acid has very little action on silver. Strong hydrochloric acid attacks silver slowly, forming silver chloride, which dissolves in the strong acid; silver can also be converted into the chloride by heating in a current of hydrogen chloride,

$$2Ag + 2HCl \rightleftharpoons 2AgCl + H_2.$$

This may be attributed to dissociation of the hydrogen chloride, the traces of chlorine produced in this way being fixed by the silver and retained as silver chloride.

Silver forms only one series of salts, in which it is univalent. It is remarkable for the large proportion of insoluble salts which it forms, a fact that is made use of for the detection of acid radicals in qualitative analysis; in this respect it stands at the opposite extreme to sodium (p. 553).

Silver-plating.

(*a*) *Electro-deposition of Silver*.—When an aqueous solution of silver nitrate is electrolysed, pure silver is deposited in a granular or crystalline form. This property is used in the SILVER VOLTAMETER (Fig. 281), where silver is deposited on the interior of a platinum bowl from a solution of silver nitrate (using a silver anode wrapped in filter-paper to maintain the strength of the solution), washed, dried, and weighed in order to measure the current; by international agreement the current which deposits 1·118 mg. of silver in one second is known as the AMPERE.

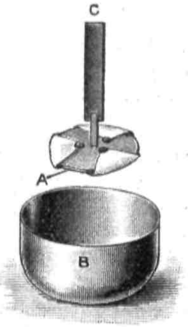


FIG. 281.—SILVER VOLTAMETER.
A=anode. *B*=cathode
C=support for anode.

(*b*) *Electro-plating*. — The earliest silver-plate known as SHEFFIELD PLATE was made by welding together copper and silver and rolling the composite metal into sheets so as to produce a silver surface on a copper base; this process has, however, been replaced by the more economical operation of ELECTRO-PLATING. The silver deposited from silver nitrate is too granular to be of any value for this purpose, but it was discovered in 1840 that a thin coherent film of silver can be deposited from a solution of **potassium argenticyanide,** $KAgC_2N_2$, prepared by adding an excess of potassium cyanide to a solution of silver nitrate,

$$AgNO_3 + 2KCN = KAgC_2N_2 + KNO_3.$$

In order to carry out the process of electro-plating, the negative pole of a battery is connected to the objects to be plated, which thus become the cathode, whilst silver plates or pieces of scrap silver are used as the anode in order to maintain the strength of the plating bath.

(*c*) *Silver Mirrors*.—Ammoniacal solutions of silver nitrate containing silver oxide, Ag_2O, dissolved in an excess of ammonia, are able to oxidise many organic compounds, *e.g.*, tartaric acid (as ammonium tartrate) and the sugars. In this process the silver oxide is reduced to silver, and if the action takes place in a glass vessel a brilliant mirror of metallic silver may be produced.

Compounds of Silver.

Silver chloride, AgCl, occurs as CHLOROARGYRITE, or HORN SILVER, sometimes in octahedral crystals, but more frequently as a horny mass of a white or grey colour. It is formed when chlorine is passed over silver at a dull red heat. The action of hydrogen chloride,

$$2Ag + 2HCl \rightleftharpoons 2AgCl + H_2,$$

is reversible, since this gas converts silver into the chloride, whilst hydrogen reduces the chloride again to the metal. On adding a soluble

chloride, *e.g.*, sodium chloride, or dilute hydrochloric acid to a solution of silver nitrate, silver chloride is precipitated as a white cloud which curdles when shaken or stirred, and darkens rapidly when exposed to light, taking on a purple colour. Silver chloride melts at 455°, forming a dark yellow liquid. It is practically insoluble in water, which dissolves only about 1·5 mg. per litre at 18°, but it dissolves to the extent of 1 part in 200 parts of concentrated hydrochloric acid; it also dissolves readily in concentrated solutions of sodium chloride and of silver nitrate. It is freely soluble in aqueous ammonia (1 part in 12·9 parts of ammonia of density 0·89), probably owing to the formation of the **ammine,** $2AgCl,3NH_3$, which can be crystallised out from the solution by slow evaporation. Liquid ammonia, on the other hand, deposits at $-40°$ the **triammine,** $AgCl,3NH_3$. This compound is also formed on passing gaseous ammonia over the dry chloride at atmospheric temperatures, but decomposes readily into the sesquiammine, which has a lower dissociation-pressure. The decomposition by heat of these compounds was used by Faraday in liquefying ammonia gas. Silver chloride also dissolves readily in solutions of sodium thiosulphate ("hypo") and of potassium or sodium cyanide.

Silver chloride is used in photography (p. 860), owing to its sensitiveness to the action of light, a property which it shares with the bromide and iodide.

Silver bromide, AgBr, obtained by precipitating a solution of the nitrate with a soluble bromide, resembles the chloride, but is less soluble in water and in aqueous ammonia, and is even more sensitive to light.

Silver iodide, AgI, is pale yellow and amorphous when freshly precipitated; it is insoluble in water and differs from the bromide and chloride in being almost insoluble in aqueous ammonia (1 part in 2500 parts of ammonia of density 0·89). It is, however, readily soluble in concentrated solutions of iodides, especially of the alkali iodides; it also dissolves freely in aqueous solutions of silver nitrate from which the double salts, $AgNO_3$, AgI, and $2AgNO_3$,AgI, can be crystallised out.

Silver iodide is dimorphous, forming hexagonal rhombohedra at ordinary temperatures, but cubical crystals above 146°; on heating through the transition-temperature at 146° the colour changes from yellow to dark red, heat is absorbed (1600 cal. per gram-molecule of AgI), and a contraction in volume of 11 per cent. takes place.

Silver fluoride, AgF, differs from the chloride, bromide, and iodide in being readily soluble in cold water; it is hygroscopic and absorbs 800 times its volume of ammonia gas.

Silver oxide, Ag_2O, separates from a solution of silver nitrate, on adding pure potassium hydroxide, as a brown precipitate which becomes nearly black when dried at 60–80°. It dissolves in aqueous ammonia, the solution on exposure to air forming **fulminating silver,** a black,

explosive compound, which has the composition NAg_3. Silver oxide when heated to 100° or exposed to sunlight loses oxygen, the conversion into metallic silver being complete at 300° ; mixed with a little caustic alkali to retain carbon dioxide, it has been used as a source of very pure oxygen. It is only very slightly soluble in water (1 part in about 50,000 parts of water at 20°), but the solution is decidedly alkaline; moist silver oxide, indeed, behaves in many ways like a **hydroxide,** AgOH, particularly with regard to organic compounds, although no compound of the composition AgOH has been isolated.

Silver peroxide, Ag_2O_2, has been obtained as a black precipitate by adding potassium persulphate to a solution of silver nitrate. It is not decomposed on heating at 100°, but at higher temperatures is resolved into its components. It oxidises aqueous ammonia to nitrogen in the cold. With dilute sulphuric acid it gives silver sulphate and oxygen,

$$2Ag_2O_2 + 2H_2SO_4 = 2Ag_2SO_4 + 2H_2O + O_2.$$

Silver carbonate, Ag_2CO_3, is a light yellow powder which is precipitated on mixing concentrated solutions of silver nitrate and an alkali carbonate in equivalent quantities. It is dissociated by heat, the action,

$$Ag_2CO_3 \rightleftharpoons Ag_2O + CO_2,$$

being reversible at temperatures up to about 220° ; at higher temperatures decomposition into silver, oxygen, and carbon dioxide occurs. When silver nitrate is added to a concentrated solution of potassium carbonate, **silver potassium carbonate,** $AgKCO_3$, is formed as a white precipitate (compare copper carbonate).

Silver sulphide, Ag_2S, is an important ore of silver under the name of ARGENTITE. It can be prepared by heating silver with sulphur or by heating metallic silver or silver chloride in a current of hydrogen sulphide; it is also formed as a blackish-brown flocculent mass by precipitating a solution of a silver salt with hydrogen sulphide. It is readily fusible, forming when cold a leaden grey mass, which is so soft that it can be cut with a knife. When strongly heated in air, it forms metallic silver, the sulphur being oxidised to sulphur dioxide.

Silver sulphate, Ag_2SO_4, is obtained by heating the finely-divided metal with concentrated sulphuric acid or by adding sulphuric acid to a concentrated solution of silver nitrate. It forms small white, lustrous crystals, and is sparingly soluble in water, which dissolves only one-ninth of its weight of the salt at 100°. It dissolves readily in ammonia owing to the formation of the soluble ammine, $Ag_2SO_4,2NH_3$.

Silver thiosulphate, $Ag_2S_2O_3$, is precipitated on adding sodium thiosulphate to a solution of silver nitrate ; it decomposes readily, as shown in the equation

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4.$$

Silver salts dissolve in sodium thiosulphate solution owing to the formation of a soluble **silver sodium thiosulphate,** $AgNaS_2O_3$, which can be prepared by evaporating a solution of silver chloride in sodium thiosulphate until it crystallises. The solubility of silver chloride in sodium thiosulphate solution is utilised in photography in the process of fixing (p. 863), and also in the extraction of silver from its ores.

Silver nitrate, $AgNO_3$, which has been known since the earliest period of alchemy under the name of LUNAR CAUSTIC, is prepared by dissolving the metal in dilute nitric acid and concentrating the solution until crystallisation occurs. It forms large, transparent, anhydrous plates, melts at a relatively low temperature (217°), and can easily be cast into sticks; in this form it is employed in surgery as a caustic. It dissolves in less than an equal weight of water at 0° and in one-ninth of its weight of water at 100°. If excess of ammonia be added to a solution of silver nitrate and the solution evaporated, crystals of the **ammine,** $AgNO_3,2NH_3$, separate.

Silver nitrate is used largely in photography and to a lesser degree in medicine and surgery. It is used as an electrolyte in the silver voltameter, but when electrolysed with a platinum instead of a silver anode it gives a black insoluble **peroxynitrate** to which the formula $2Ag_3O_4,AgNO_3$ has been assigned. This decomposes slowly in warm water and rapidly on boiling, leaving a black residue of silver peroxide, Ag_2O_2 (p. 851),

$$Ag_7NO_{11} = AgNO_3 + 3Ag_2O_2 + O_2.$$

Insoluble Salts of Silver.

In addition to the compounds described above, a large number of salts of silver which are insoluble or sparingly soluble in water can be prepared as precipitates by adding a soluble salt of the acid to a soluble salt of silver.

TABLE 91.—INSOLUBLE SALTS OF SILVER.

Name.	*Formula.*	*Colour.*
Silver oxide	Ag_2O	Black
„ sulphide	Ag_2S	Black
„ chloride	$AgCl$	White (turning to purple)
„ bromide	$AgBr$	Pale yellow
„ iodide	AgI	Yellow
„ cyanide	$AgCN$	White
„ sulphocyanide	$AgCNS$	White
„ ferrocyanide	$Ag_4FeC_6N_6,H_2O$	White (turning to blue)
„ ferricyanide	$Ag_3FeC_6N_6$	Yellow
„ nitrite	$AgNO_2$	Colourless crystals.
„ hyponitrite	$Ag_2N_2O_2$	Yellow
„ chromate	Ag_2CrO_4	Dark red

TABLE 91.—INSOLUBLE SALTS OF SILVER (*continued*).

Name.	*Formula.*	*Colour.*
Silver borate . .	$Ag_2B_2O_4,H_2O$	White (turning to yellow and black)
,, phosphate .	Ag_3PO_4	Yellow
,, sulphite . .	Ag_2SO_3	White
,, thiosulphate .	$Ag_2S_2O_3$	White

The soluble salts of silver include the fluoride, AgF, the nitrate, $AgNO_3$, the sulphate, Ag_2SO_4, the chlorate, $AgClO_3$, and double salts such as potassium argenticyanide, $KAgC_2N_2$, and sodium silver thiosulphate, $NaAgS_2O_3$, but they are comparatively few in number.

Detection and Estimation of Silver.

Silver salts when heated on charcoal with sodium carbonate in a reducing flame give lustrous white beads of metallic silver. A solution of a silver salt gives with hydrochloric acid a white precipitate of **silver chloride,** AgCl, which is insoluble in dilute nitric acid but soluble in ammonia; hydrogen sulphide precipitates the black **silver sulphide,** Ag_2S, which dissolves readily in hot nitric acid.

Silver is estimated gravimetrically by precipitation as **silver chloride,** AgCl, or, as in assaying, by CUPELLATION, when the base metals are separated by oxidation in a muffle furnace, using a bone-ash cupel to absorb the oxides, the pure silver being left as a bead and weighed as **metallic silver.**

Silver is also estimated volumetrically by precipitation as **silver chloride** with a standard solution of sodium chloride (p. 154), or as **silver thiocyanate,** AgCNS, by means of ammonium thiocyanate, using ferric alum as an indicator (Volhard's method).

The atomic weight of silver is based upon Stas' determinations of the ratios KCl : $KClO_3$, KCl : AgCl, and Ag : AgCl (p. 292); in more recent experiments the ratios

$$Ag_2SO_4 : 2AgCl,\ Ag : AgNO_3,\ \text{and}\ LiClO_4 : LiCl : AgCl : Ag$$

have been determined.

79. GOLD. Au = 197·2.

Occurrence.

Gold nearly always occurs in the metallic form as NATIVE GOLD, the only natural compound being an alloy or compound with tellurium, the **telluride,** $AuTe_2$. Native gold always contains silver, its composition varying from 65 to 99 per cent. of gold with 35 to 0·4 per cent. of silver, according to the source and locality from which it is obtained. Considerable quantities of gold are also obtained during the refining of lead (p. 691) and copper (p. 830) and in the purification of silver (p. 847).

Sources.

Native gold is distributed widely, as in the case of the Transvaal mines, in veins or reefs of quartz intersecting other rocks, the particles of gold being usually so small as to be invisible to the eye. The disintegration of such rocks under the action of water gives rise to alluvial deposits of gold in the sand or gravel of river-beds. Thus, the gold of California is extracted mainly from gravels and sand deposited alluvially, the beds varying in thickness from 80 to 250 feet; of recent years, however, true quartz rock has been mined in California for gold.

The proportion of gold in the ore is usually very small, varying from 1 part in 50,000 in gold quartz to 1 part in 1 to 15 millions in alluvium; but nuggets of gold, formed by the segregation and welding together of gold-particles in the river-beds, have been found, especially in Australia, weighing from a few ounces to 184 lb.

Extraction of Gold.

(*a*) *Washing and Amalgamation.*—The coarse particles of alluvial gold can be separated by taking advantage of its high density, varying from 19 to 17 according to the proportion of silver which it contains, as compared with the low density, about 2·7, of the sand or gravel with which it is mixed. For this purpose the material is washed in a " pan " or " cradle " consisting of an inclined trough mounted on rockers, the trough being furnished with bars of wood placed across it to hold back the particles of gold as they settle out from the sand or gravel. Finer particles may be retained during washing by making use of mercury, which forms an AMALGAM from which the gold can be recovered by distillation.

(*b*) *Cyanide Process.*—The very finely divided gold of the Transvaal is dissolved in a dilute solution of potassium or sodium cyanide (pp. 479 and 789) in presence of atmospheric oxygen. The action which takes place may be expressed by the equation

$$4Au + 8KCN + O_2 + 2H_2O = \underset{\text{Potassium aurocyanide}}{4KAuC_2N_2} + 4KOH.$$

The metal is precipitated by passing the solution through wooden boxes containing zinc turnings;

$$2KAuC_2N_2 + Zn = K_2ZnC_4N_4 + 2Au.$$

The precipitated gold is treated with dilute sulphuric acid to remove any zinc and after washing and drying is melted with a flux. The resulting metal has a fineness of 850 to 900 (*i.e.*, 85 to 90 per cent.). The gold may also be deposited electrolytically, using an iron anode and a lead cathode; the iron anodes are converted into Prussian blue, $Fe_7C_{18}N_{18}$, and the lead cathodes on which the gold is deposited are cupelled and the gold recovered.

(*c*) *Chlorination Process.*—This process is used mainly to separate

gold from pyrites or from ores containing gold as telluride. The ore is roasted to remove sulphur and arsenic; it is then moistened with water and placed in tubs furnished with false bottoms and lined with pitch, and a stream of chlorine is passed in from below so as to displace the air. After twenty-four to thirty-six hours the material is extracted with water and the metal precipitated from the chloride by means of ferrous sulphate,

$$2AuCl_3 + 6FeSO_4 = 2Au + Fe_2Cl_6 + 2Fe_2(SO_4)_3.$$

The gold settles as a fine powder which is washed to remove salts of iron and melted to an ingot.

Chlorination may also be effected by a wet process in revolving lead-lined drums in which the ore is mixed with bleaching powder and dilute acid; in this case the gas acts under pressure, and chlorination is complete in a very short time ($1\frac{1}{2}$ to 2 hours). Bromine is frequently used in place of chlorine, its action giving rise to a soluble gold bromide.

Refining of Gold.

(*a*) *Fineness of Crude Gold.*—The gold extracted by the above processes is invariably accompanied by silver, the silver and gold together generally accounting for 99·6 to 99·8 per cent. of the crude bullion. The proportion of silver may vary from about 15 per cent. in Germany to 10 per cent. in California, 5 per cent. in the Transvaal, and as little as 0·4 per cent. in certain parts of Australia.

(*b*) *Parting by Chlorine.*—The silver can be removed from the gold very simply by melting the bullion in a clay crucible (glazed inside by means of borax) and passing chlorine gas through it; the chlorine combines with the silver to form silver chloride, which floats to the surface of the metal, whilst other chlorides, such as those of zinc, bismuth, antimony, and arsenic, are volatilised away. At the high temperature employed, gold does not form a chloride (gold chloride is decomposed above 200°), so that it remains as metal at the bottom of the crucible. The fineness of the metal thus obtained varies from 991 to 997 per 1000 parts.

(*c*) *Parting by Acids.*—If the proportion of gold does not exceed 1 part of gold to 2 parts of silver, the silver can be dissolved away by means of either nitric or sulphuric acid, the gold remaining unchanged. If necessary, silver is added so as to make the proportion suitable; the alloy is then granulated and heated either with nitric acid (density 1·2 to 1·4) or with concentrated sulphuric acid (density 1·85), and the residue of gold is washed and melted into an ingot.

(*d*) *Electrolytic Refining.*—Gold and silver can be separated electro lytically. The small proportion of gold in silver bullion may be recovered by electrolysis in a solution of silver nitrate, when the gold is left behind in the anode slime (compare p. 831). Gold bullion, on the other hand, may be refined by electrolysis in a hot solution of auric

chloride made strongly acid with hydrochloric acid and containing a little sulphuric acid to precipitate lead as sulphate ; the silver and lead are converted into a slime of AgCl and $PbSO_4$, whilst the gold is deposited in a pure state at the cathode, leaving behind in solution any platinum which may be present. This process has the advantage that there is practically no loss of precious metal, that the gold finally obtained is of a high degree of purity (99·9 per cent.), and that the platinum which it contains can be separated and recovered.

Properties of Gold.

(*a*) *Physical Properties.*—Gold is a bright yellow, lustrous metal crystallising in forms derived from the cubic system. Its density is 19·3, and it is therefore impossible effectively to counterfeit it. It melts at 1063°, and this temperature is so well defined that it has been used extensively as a " third point " (in addition to the boiling-point and freezing-point of water) for standardising pyrometers. Gold is very malleable and ductile ; it can be beaten out into leaf of a thickness of 0·0001 mm. and 1 gram of the metal can be drawn out into 3240 metres of wire. Next to silver and copper, gold is the best conductor of heat and electricity.

(*b*) *Chemical Properties.*—Gold is one of the most resistant among metals to the action of acids, being dissolved only by aqua regia, or other acid liquids in which chlorine, bromine, or iodine is produced, and by selenic acid. It is not affected by oxygen or water, nor by fusion with potassium chlorate, but is attacked by fused alkalies or nitrates. It is attacked rapidly by chlorine and by bromine at atmospheric temperatures and is dissolved by an aqueous solution of potassium or sodium cyanide in presence of air. It is dissolved readily by mercury, forming an AMALGAM which becomes solid when 15 per cent. of gold is present.

(*c*) *Colloidal Gold.*—A *red* solution (or more strictly a suspension) of colloidal gold is obtained by reducing a dilute solution of a gold salt with formaldehyde ; on adding alcohol the gold is precipitated in a form which redissolves in water. A *blue* colloidal solution is obtained when hydrazine hydrate is used as the reducing agent. Carbon monoxide, passed into a very dilute solution of a gold salt, produces a *purple* coloration, due to colloidal gold. On passing an electric arc under water between gold wires, *reddish-purple* and *blue* colloidal solutions of gold are obtained. The colour of the solution depends, however, only on the size of the particles of gold ; different colours may therefore be obtained with the same reducing agents, or identical colours with different reducing agents. The addition of an electrolyte to these solutions causes the precipitation of metallic gold.

(*d*) *Purple of Cassius.*—When stannous chloride is added drop by drop to a solution of a gold-salt a purple-violet precipitate is obtained, known as PURPLE OF CASSIUS, which probably consists of stannic

hydroxide coloured by colloidal gold. A similar precipitate is obtained by using mercurous in place of stannous chloride, or by distilling an alloy of gold and tin in the air, when the stannic oxide is coloured purple. It is used in the preparation of ruby glass and in colouring porcelain.

(*e*) *Alloys of Gold.*—Pure gold is too soft to be employed in coinage; in English coins an alloy of 22 parts of gold and 2 parts of copper, known as 22 carat * gold, and containing 91·67 per cent. of gold, with 8·33 per cent. of copper in solid solution, is employed; this has a red colour. In Australian coinage, silver takes the place of copper, and the metal is of a pale yellow colour.

An alloy of gold with aluminium containing 78 per cent. of gold and 22 per cent. of aluminium melts at 1060° (gold melts at 1063° and aluminium at 659°); the alloy has an intense ruby colour and is regarded as a definite chemical compound of the formula $AuAl_2$.

(*f*) *Valency.*—Gold forms two classes of compounds, namely, AUROUS COMPOUNDS of the type AuCl, in which the metal is univalent, and AURIC COMPOUNDS of the type $AuCl_3$, in which the metal is tervalent; in this respect it resembles thallium. The aurous salts, however, show a marked resemblance to the bivalent palladous and platinous salts, whilst the auric salts show a similar resemblance to the quadrivalent palladic and platinic salts.

AUROUS COMPOUNDS.

Aurous chloride, AuCl, is formed on heating auric chloride, $AuCl_3$, at 180°. It is a yellow or white powder which is insoluble in cold water, but is decomposed by hot water, forming soluble auric chloride and metallic gold,

$$3AuCl = AuCl_3 + 2Au.$$

Liquid ammonia acts on aurous chloride at − 28° to form the **ammine,** $AuCl,12NH_3$, which loses ammonia on warming, forming the **triammine,** $AuCl,3NH_3$; this compound is not decomposed until a temperature of 180° is reached.

Aurous bromide, AuBr, also absorbs ammonia gas, forming an **ammine,** $AuBr,2NH_3$, which is decomposed by water, forming ammonium bromide and gold (compare the decomposition of $CuCl_2,2NH_3$, p. 840).

Aurous iodide, AuI, separates as a yellowish-white powder on adding potassium iodide o a solution of auric chloride, iodine being liberated (compare cuprous iodide),

$$AuCl_3 + 3KI = AuI + I_2 + 3KCl.$$

It is also formed when metallic gold is heated with dry iodine between 50° and 114°. It is an unstable compound and when heated is decom-

* The number of carats shows the proportion of pure gold in 24 parts, 24 carat gold being the pure metal.

posed into its components. With gaseous ammonia it forms the compounds $AuI,6NH_3$ and AuI,NH_3, which are decomposed by water.

Aurous oxide, Au_2O.—On reducing potassium aurichloride, $KAuCl_4$, with sulphur dioxide at 0° until a colourless solution is obtained and then adding potassium hydroxide, aurous hydroxide, $AuOH$, is precipitated as a violet-black powder ; on drying the hydroxide at 100°, the oxide, Au_2O, is obtained. It decomposes at 250°,

$$2Au_2O = 2Au_2 + O_2,$$

and when acted on by hydrochloric acid gives gold and auric chloride.

Potassium aurochloride, $KAuCl_2$, is formed when potassium aurichloride, $KAuCl_4$, is heated. It forms a yellow mass which is decomposed by water into gold, potassium chloride, and auric chloride.

Potassium aurocyanide, $KAuC_2N_2$, is formed when finely-divided gold is dissolved by potassium cyanide in presence of air. It is largely used in gilding and can be prepared conveniently by dissolving gold in aqua regia, so as to form a solution of auric chloride, adding ammonia, which precipitates "fulminating gold," washing the latter and dissolving it in a boiling solution of potassium cyanide ; on filtering the solution and cooling, the aurocyanide separates in crystals.

Aurous sulphide, Au_2S, is obtained as a black precipitate (mixed with gold and sulphur) on passing hydrogen sulphide into a *hot* solution of auric chloride, or by passing the same gas into a solution of aurous cyanide in potassium cyanide and then acidifying ; it is not dissolved by hydrochloric or sulphuric acid, but is readily dissolved by potassium cyanide.

AURIC COMPOUNDS.

Auric Chloride, $AuCl_3$.—Anhydrous auric chloride is obtained by passing chlorine over gold-leaf at 300 ° ; it forms a brown crystalline mass which is deliquescent and dissolves readily in water, forming a solution from which orange-red crystals of the **dihydrate,** $AuCl_3,2H_2O$, separate on concentrating ; the same salt is obtained by evaporating a solution of gold in aqua regia and drying the product at 100°, but some decomposition to aurous chloride occurs in the process. Auric chloride begins to dissociate below 100°,

$$AuCl_3 = AuCl + Cl_2,$$

but it can be sublimed without decomposition in a current of chlorine at temperatures up to 1100°.

When a solution of gold in aqua regia containing an excess of hydrochloric acid is evaporated and allowed to stand over quicklime, long yellow needles of **aurichloric acid,** $HAuCl_4,4H_2O$, compare H_2PtCl_6, separate ;

$$Au + HNO_3 + 4HCl = HAuCl_4 + NO + 2H_2O.$$

This substance is deliquescent and loses its acid at 100°, but it yields a

series of well-defined crystalline salts known as AURICHLORIDES. Thus, **potassium aurichloride,** $KAuCl_4,2H_2O$, **sodium aurichloride,** $NaAuCl_4,2H_2O$, and **ammonium aurichloride,** NH_4AuCl_4, are obtained by simply crystallising together equimolecular proportions of their constituent chlorides. They are less soluble and less deliquescent than auric chloride, and, like the acid, are frequently sold in place of this compound for toning silver prints in photography (p. 863). The corresponding **nitrates,** $HAu(NO_3)_4$ and $KAu(NO_3)_4$, have been prepared, although auric nitrate is not known.

Auric iodide, AuI_3, is unstable and decomposes to form aurous iodide and iodine; a series of auri-iodides is, however, known.

Auric oxide, Au_2O_3, is generally stated to be obtained by carefully heating the hydroxide, $Au(OH)_3$, but it is doubtful whether the brown powder so obtained is the pure oxide. An explosive compound, long known as FULMINATING GOLD, is obtained when auric chloride is precipitated by ammonia. It can be represented by the formula $Au_2O_3,4NH_3$. When detonated, nitrogen is set free and metallic gold is recovered,

$$Au_2O_3 + 2NH_3 = N_2 + 2Au + 3H_2O,$$

two of the molecules of ammonia being superfluous for this decomposition. Fulminating gold can also be regarded as containing an **auric nitride,** AuN, combined with ammonia and with water; similar compounds of **aurous nitride,** Au_3N (compare Ag_3N), can be prepared by digesting aurous oxide with ammonia.

Auric hydroxide or **Auric acid,** $Au(OH)_3$, is obtained by heating a solution of auric chloride with magnesia and washing the resulting precipitate with dilute nitric acid, which removes the excess of magnesia but does not dissolve the gold hydroxide. This is remarkable in behaving as an acid rather than as a base; thus, it is insoluble in water and in dilute acids, but is dissolved by alkaline hydroxides. It dissolves slightly in concentrated sulphuric and nitric acids, forming probably an acid sulphate, or the acid **nitrate,** $HAu(NO_3)_4$, already referred to, but the hydroxide is reprecipitated unchanged on adding water. It dissolves, however, in hydrochloric acid to form aurichloric acid,

$$Au(OH)_3 + 4HCl = HAuCl_4 + 3H_2O.$$

When kept over phosphoric anhydride it loses water and is converted into a chestnut-coloured powder, which has the composition $AuO(OH)$ and is known as **auryl hydroxide** or **meta-auric acid,**

$$Au(OH)_3 = AuO{\cdot}OH + H_2O.$$

This is the parent substance of a series of salts which are formed by dissolving auric hydroxide in solutions of alkalies; thus, potassium hydroxide gives **potassium meta-aurate,** $AuO{\cdot}OK,3H_2O$, which forms yellow needles and is easily soluble in water; the solution has an

alkaline reaction owing to hydrolysis occurring. Salts of normal auric acid are not known.

Auric sulphide, Au_2S_3, cannot be prepared by the action of hydrogen sulphide on auric chloride, since this gives aurous sulphide, Au_2S; it has been obtained by the action of dry hydrogen sulphide on lithium aurichloride at − 10°, and is soluble in solutions of alkali sulphides, forming aurisulphides, *e.g.*, K_3AuS_3, which readily changes into K_3AuS_2, a derivative of aurous sulphide Au_2S.

Detection and Estimation of Gold.

(*a*) *Detection.*—When a compound of gold is heated before the blowpipe a yellow bead of metallic gold is obtained which dissolves in aqua regia; the solution is reduced to metal by sulphurous acid, ferrous sulphate, or stannous chloride. The most delicate test consists in adding the boiling solution supposed to contain gold to a little concentrated stannous chloride; if gold is present the precipitated stannous hydroxide has a purple colour (purple of Cassius); 1 part of gold in 100,000,000 parts of water can be thus detected.

(*b*) *Assay of Gold Ores.*—The ore is fused with red lead or litharge, charcoal, sodium carbonate, and a little iron; a button of lead is obtained which contains all the gold and silver present and is cupelled. The residual bead of silver and gold is treated with nitric acid, which removes the silver and leaves the gold. Special precautions have to be observed in order to obtain accurate results.

(*c*) *Atomic Weight.*—The atomic weight of gold is based upon determinations of the ratios $AuCl_3 : 3AgCl$, $KAuBr_4 : Au : 4AgBr$, $Au : KBr$, etc.

Photography and Photochemistry.

Chemical Changes Produced by Light.

It has long been known that many chemical changes are promoted by the action of light, *e.g.*, the bleaching of colours which are not "fast" to light, and the reduction, by the chlorophyll of green leaves, of carbon dioxide to produce the various carbon compounds which are found in plants. Of these changes, the combination of hydrogen with chlorine (p. 275) was selected by Bunsen and Roscoe as a means of measuring the intensity of light in an ACTINOMETER, which was designed to record the contraction that takes place when these gases unite together in presence of water. The intensity of light has also been measured by means of EDER'S SOLUTION, a mixture of mercuric chloride and ammonium oxalate which is decomposed by light as shown in the equation:

$$2HgCl_2 + (NH_4)_2C_2O_4 = Hg_2Cl_2 + 2NH_4Cl + 2CO_2.$$

Action of Light on Silver Salts.

On prolonged exposure to light, silver chloride yields a dark lavender-coloured product and liberates from 5 to 10 per cent. of its chlorine the action is reversible and comes to a standstill at a definite concentration of chlorine corresponding with the intensity of the light The coloured product was formerly regarded as a "sub-chloride," *e.g.* Ag_2Cl, but is now believed to be a solution of colloidal silver in solid silver chloride with a small quantity of free silver. The darkening of silver salts by light is promoted by the presence of oxidisable materials; thus paper soaked in a solution of silver nitrate blackens on exposure to light through reduction of the nitrate to metallic silver. In a similar manner a mixture of silver chloride and silver citrate, precipitated together from solution, is used extensively in presence of gelatine or collodion for coating PRINTING-OUT PAPERS, on which a coloured picture can be produced by exposure to light. Printing-papers provide the commonest type of actinometer, namely, one in which the intensity of light is measured by the time taken to produce a standard tint on a piece of the printing-paper.

The Latent Image and its Development.

Long before a silver salt is coloured by exposure to light, it is possible by various processes of DEVELOPMENT to detect a change, which is described as the formation of a LATENT IMAGE. Thus, a film of silver iodide which has been exposed to light for a very brief period receives an impression which can be "developed," or rendered visible, by exposing the film to the vapour of mercury, as in the DAGUERREOTYPE PROCESS invented in 1839. The latent image can be made visible even more effectively by means of a CHEMICAL DEVELOPER, *e.g.*, a solution of silver nitrate and gallic acid (Fox Talbot, 1841), which deposits silver on the "exposed" portions of the iodide-film. The development of a latent image is the essential feature of all those processes of PHOTOGRAPHY in which only a short exposure to light is practicable, as in the camera, in gaslight printing, etc. In the early photographic processes a WET PLATE was prepared by immersing a film of collodion successively in solutions of potassium iodide and of silver nitrate; in the modern DRY PLATE the silver salt is precipitated as an EMULSION * in gelatine, without any excess of silver nitrate, and the latent image is developed by a reducing agent (*e.g.*, potassium ferrous oxalate, pyrogallol, hydroquinone, etc.) which liberates metallic silver from those grains of silver salt which have been exposed to light, whilst attacking only very slowly those grains which have not been exposed. Although it is a more stable compound than the iodide, silver bromide has been found to be by far the most sensitive silver

* This term is here used in an exceptional manner to describe a suspended solid instead of a dispersed liquid.

salt to use in the gelatine emulsion. The sensitiveness of the plate can be increased by a process of RIPENING the warm emulsion, whereby the average size of the grains is increased and may attain 6 or 8 cm.$^{-4}$ in diameter, before spreading it on the plate and allowing it to set and dry; during this process the grains become definitely crystalline, exhibiting various forms characteristic of the cubic system. The ordinary dry plate is most sensitive to light in the blue region of the spectrum; its sensitiveness to the green, yellow, and red regions of the spectrum may be increased by staining the grains with various dyes. Conversely, the sensitiveness of the plate to light may be reduced by bathing it in certain dyes, of which safranine is one of the most potent; if this is done after exposure, the latent image can then be developed in a fairly bright light without fogging the plate.

It has been calculated that the quantity of light-energy required to create a latent image on a grain of silver bromide is less than that required to decompose a single molecule into its elements; the change in the material is therefore very slight and may be merely the loss of an electron. During the early stages of exposure ("under-exposure") the DENSITY of the developed image, *i.e.*, the logarithm of the ratio of incident to transmitted light, increases only slowly, and is approximately proportional to the EXPOSURE (intensity × time); there is then a considerable period, during which the density increases in a linear relation to the *logarithm* of the exposure ("correct exposure period" of HURTER and DRIFFIELD); the increase of density with exposure then diminishes ("over-exposure"), so that the contrast between different portions of the plate tends to disappear. When exposure is prolonged still further, *e.g.*, to 1000 times the normal, REVERSAL or SOLARISATION takes place; a plate which has been treated in this way may still be made to give, with certain very weak developers, the usual NEGATIVE picture, in which the exposed parts are dark and the unexposed parts are light; but with the ordinary alkaline developers a POSITIVE picture results, perhaps because the latent image has been converted into stable and insensitive products of decomposition as a result of excessive exposure to light, whilst the less-exposed portions of the plate have acquired a normal latent image.

Development, Printing, Fixing, Toning, etc.

The essential feature of the process of developing a film or plate after exposure in a camera consists in the selective reduction of the silver haloid to silver in the grains which have been exposed to light, *e.g.*, as in the balanced action:

$$\underset{\text{Potassium ferrous oxalate}}{K_2Fe(C_2O_4)_2} + AgBr \rightleftharpoons \underset{\text{Potassium ferric oxalate}}{KFe(C_2O_4)_2}^{*} + Ag + KBr.$$

When the image has been developed sufficiently the negative picture

* Potassium ferric oxalate usually crystallises as $K_3Fe'''(C_2O_4)_3$, *i.e.* $KFe(C_2O_4)_2 + K_2C_2O_4$. It is noteworthy that this salt is green, whilst potassium ferrous oxalate is yellow.

is FIXED by dissolving out the unchanged silver salt in a bath of sodium thiosulphate or "hypo":

$$Na_2S_2O_3 + AgBr = NaAgS_2O_3 + NaBr.$$

A POSITIVE picture is then produced on paper or on glass (*e.g.*, for lantern slides) by CONTACT PRINTING or in an enlarging lantern, either with direct production of a visible image on a printing-out paper or by development of the latent image produced by a short exposure to light of "gaslight" or "bromide" papers. The TONING of the positive picture, which is often carried out simultaneously with fixing, consists usually, in the case of printing-out papers, in a partial displacement of the silver of the visible image by gold in order to improve the colour of the picture, *e.g.*,

$$KAuCl_4 + 3Ag = Au + 3AgCl + KCl;$$

the best toning baths contain a gold salt with a thiocyanate as a reducing agent to facilitate the precipitation of the gold. In developed prints, however, the most usual method of toning is by conversion of the silver of the image into sulphide.

A negative in collodion which is too weak to give a good print may be INTENSIFIED by depositing more silver from a developer containing silver nitrate. In gelatine negatives the changes employed are usually such as to give a duplicate deposit of metal, *e.g.*,

$$Ag + HgCl_2 = AgCl + HgCl$$

$$\begin{cases} AgCl + K_2Fe(C_2O_4)_2 = Ag + KCl + KFe(C_2O_4)_2 \\ HgCl + K_2Fe(C_2O_4)_2 = Hg + KCl + KFe(C_2O_4)_2; \end{cases}$$

in this case the deposit of silver is supplemented by an equal number of atoms of metallic mercury. In another process, which can be applied to collodion negatives, two equivalents of silver chloride are formed by the action of cupric chloride, and, on reduction with potassium ferrous oxalate, give rise to two additional equivalents of silver, thus:

$$\begin{cases} Ag + CuCl_2 = AgCl + CuCl \\ CuCl + 2AgNO_3 = Ag + AgCl + Cu(NO_3)_2 \end{cases}$$

$$Ag + 2AgCl + 2K_2Fe(C_2O_4)_2 = 3Ag + 2KCl + 2KFe(C_2O_4)_2.$$

Conversely, a negative which is too dense is sometimes REDUCED by removing some of the silver, *e.g.*, by the action of a persulphate:

$$2Ag + K_2S_2O_8 = Ag_2SO_4 + K_2SO_4,$$

or by partial reconversion to a chloride, *e.g.*,

$$Ag + FeCl_3 = AgCl + FeCl_2,$$

and removal of the chloride in a fixing bath.

Other Photographic Processes.

Apart from silver salts, the principal light-sensitive materials used in photography are salts of iron and compounds of chromium.

(*a*) The reduction of ferric salts in presence of organic matter gives an invisible ferrous image which can be developed by various processes,

of the same general type as the "toning" of a silver print. Thus in the PLATINOTYPE PROCESS the printing paper is coated with ferric oxalate and potassium platinochloride, exposed, and developed with potassium oxalate, giving a permanent picture in metallic platinum. These actions may be represented by the following equations :

(i) *Printing* $\underset{\text{Ferric oxalate}}{Fe_2(C_2O_4)_3} = \underset{\text{Ferrous oxalate}}{2FeC_2O_4} + 2CO_2$.

(ii) *Developing* $FeC_2O_4 + K_2PtCl_4 = 2KCl + FeCl_2 + Pt + 2CO_2$
and
Fixing $Fe_2(C_2O_4)_3 + 3K_2C_2O_4 = 2K_3Fe(C_2O_4)_3$,

followed by baths of weak hydrochloric acid to remove iron salts. In the ordinary BLUE PRINTS the coating contains a mixture of ferric salts with potassium ferricyanide, which acts as a developer of the ferrous image formed on exposure to light; the exposed print is developed in water, giving a print coloured with Prussian blue.

(*b*) The reduction of potassium dichromate by exposure to light in presence of gelatine, glue, or gum gives a pale brown product, perhaps CrO_2, which is taken up by the gelatine, glue, or gum, and renders it insoluble by a process analogous to the tanning of leather. The unexposed part of the film can then be washed away with hot water. In the CARBON PROCESS of printing the dichromate and gelatine are coloured by various pigments, which are retained only in the exposed part of the film, giving a permanent picture of almost any desired tint. In COLLOTYPE printing the selective absorption of greasy printing inks by the exposed areas (after wetting the film) makes it possible to use the film directly in a printing-press. In the HALF-TONE PROCESS a print in dichromated gelatine is made on a plate of copper or zinc, the image having been broken up into tiny dots by a ruled glass screen in making the negative in the camera ; the unexposed areas of the film are washed away with water, and the bare portions of the metal plate are then etched with ferric chloride to produce a half-tone block, which can be inked and used for the reproduction of pictures in the printing-press.

CHAPTER XLIV

THE MERCURY GROUP

Atomic Number.	*Element.*	*Symbol.*		*Atomic Weight.*
30	Zinc	Zn	=	65·37
48	Cadmium	Cd	=	112·40
80	Mercury	Hg	=	200·6

Classification.

The three elements, zinc, cadmium, and mercury, follow immediately after the three coinage metals, copper, silver, and gold, and, like them, form a natural group of metals. They do not form a triad, since there is a gap of 18 between the atomic numbers of zinc and cadmium, and of 32 between cadmium and mercury, the corresponding differences in atomic weight being 47·0 and 88·2; these inequalities are due to the interposition of the elements of the rare earths between cadmium and mercury in addition to the ordinary homologues of the elements from zinc to cadmium.

In addition to the relationship existing between the three members of the family, attention may be directed to points of resemblance between zinc and magnesium (p. 614), between the bivalent compounds of zinc and copper as consecutive elements of the transition-series (p. 835), and finally to the striking but unexpected resemblance between mercury and copper, lying along a steep diagonal in the periodic table.

Physical Properties.

The physical properties of these elements are shown with those of magnesium in the following table:

TABLE 92.—PHYSICAL PROPERTIES OF THE ELEMENTS OF THE MERCURY GROUP.

	Density.	*Melting-point.*	*Boiling-point.*
Mg	1·75	650°	1120°
Zn	7·1	419°	918°
Cd	8·6	321°	778°
Hg	13·6	− 39°	357°

* With gallium, indium, and thallium.

Two special characteristics of the elements of this group are the volatility of the three metals and their splendid spectra.

(*a*) *Boiling-points.*—Zinc, cadmium, and mercury can all be distilled below 1000°. The boiling-point falls as the atomic weight of the metal increases, so that mercury can be distilled in a glass vessel and has an appreciable vapour pressure (0·02 mm.) even at atmospheric temperatures. Even zinc and cadmium, however, distil almost as readily as potassium and sodium, with the result that the elements of these two groups include the majority of the metals of which the vapour densities have been determined directly.

(*b*) *Spectra.*—Of all the elements, cadmium is probably that which forms the most perfect spectrum, including the following lines:

Colour.	*Wave-length.*
Cadmium red	6438×10^{-8} cm.
,, green	5086
,, blue	4800 and 4678

The first three lines are of remarkable purity and power. The red cadmium line has been used as a standard of length from which the standard metre could be reproduced with accuracy if the original bar on which it is engraved were destroyed. The green and blue lines are similar in their characteristics and have been used extensively as sources of monochromatic light.

The mercury spectrum is dominated by a green line, 5461, which has displaced sodium as the most convenient monochromatic light for optical measurements in the laboratory, but there is also a yellow doublet, 5769, 5790, and an extremely powerful violet line, 4359, which have all been employed in similar work.

The zinc spectrum contains a red line, 6364, and three blue lines, 4811, 4722, and 4680, which can be used as sources of monochromatic light.

Chemical Properties of the Group.

(*a*) *Valency.*—The typical valency of this group is 2, the principal compounds being bivalent, as for instance in:

ZnO	$ZnCl_2$	$ZnSO_4$	$Zn(NO_3)_2$
CdO	$CdCl_2$	$CdSO_4$	$Cd(NO_3)_2$
HgO	$HgCl_2$	$HgSO_4$	$Hg(NO_3)_2$.

Mercury is, however, distinguished from cadmium and zinc by forming a full series of univalent salts, *e.g.*, Hg_2Cl_2, Hg_2SO_4, and $HgNO_3$. In this respect, and in many of its other chemical properties, mercury shows a resemblance to copper, which could not be predicted from its position in the periodic table.

(*b*) *Oxidation.*—The gradation of chemical properties in these

elements can be shown conveniently by tabulating them with the coinage metals in three groups, as follows:

	(ii)	**(i)**
	Cu	**Zn**
	Ag	Cd
(iii)	Au	Hg

(i) *Zinc* and *cadmium* are base metals which burn in air and dissolve readily in dilute acids.

(ii) *Copper, mercury,* and *silver* are insoluble in most dilute acids, but dissolve in oxidising acids such as nitric acid or concentrated sulphuric acid, liberating not hydrogen, but oxides of nitrogen or sulphur dioxide. These three metals are also of interest as stages in the transition from the base to the noble metals, the oxides becoming progressively less stable in the series Cu_2O, CuO, HgO, Ag_2O. Mercury, which oxidises at 300°, but is set free again when its oxide is heated to 500°, occupies an intermediate position between the base and noble metals.

(iii) *Gold,* the remaining element shown in the scheme, is in all respects a noble metal, since it is not attacked by oxygen under any conditions, and can only be dissolved by making use of a chlorinating agent such as aqua regia or a specially powerful oxidising acid such as selenic acid.

(*c*) *Extraction of Metals.*—Although the bivalent oxides of beryllium, magnesium, calcium, strontium, and barium cannot be reduced by carbon even at a high temperature, the oxides of zinc, cadmium, and mercury can all be reduced by carbon; but the ease with which this is accomplished increases progressively from zinc to mercury, far less energy having to be supplied in the case of mercury than of zinc. This is shown by the following table, which gives the heats of formation of the oxides of some of these metals:

Oxide.	*Heat of Formation.*	
MgO	143,000 calories	Not reducible by carbon.
ZnO	85,000 ,,	Reducible by carbon at high temperatures, but not by hydrogen.
CdO	30,400 ,,	Reducible by carbon at a red heat, and by hydrogen above 270°.
HgO	21,000 ,,	Loses oxygen when heated alone.

(*d*) *Abnormal Properties of Mercury.*—The properties of mercury are in many respects abnormal. Not only does it form two series of salts instead of one, but a large number of compounds are known in which mercury is ready to occupy a place in the acid radical, as in the case of **potassium mercuri-iodide,** K_2HgI_4; this tendency also exists, but in a much lesser degree, in the case of cadmium. It is perhaps on account of this neutral character of mercury that mercuric

chloride, $HgCl_2$, although soluble in water, is not an electrolyte. Again mercury has the power of entering into organic compounds, and of displacing hydrogen from derivatives of ammonia to form compounds such as NHg_2Cl without taking up the normal part of a metal in a metallic salt.

30. ZINC. Zn = 65·37.

Occurrence.

The principal ore of zinc is **zinc sulphide** or BLENDE, ZnS, a mineral which is found in veins in various parts of England and Wales, in Belgium, in Silesia, and in very large quantities at Broken Hill, in Australia, where it is mixed with galena, PbS. Less important ores are:

CALAMINE,	$ZnCO_3$	
SILICEOUS CALAMINE,	Zn_2SiO_4,H_2O	
ZINCITE or RED ZINC ORE,	ZnO	
ZINC SPINEL or GAHNITE,	$ZnAl_2O_4$	Two members of the spinel group of minerals.
FRANKLINITE,	$ZnFe_2O_4$	

Preparation of Metallic Zinc.

The extraction of zinc from its ores depends on the conversion of the sulphide or carbonate into oxide, and the reduction of the oxide by distillation with carbon.

(*a*) *Roasting.*—Calamine is roasted to convert the carbonate into oxide,

$$ZnCO_3 = ZnO + CO_2.$$

The roasting of blende sets free large quantities of sulphur dioxide,

$$2ZnS + 3O_2 = 2ZnO + 2SO_2;$$

it is therefore now carried out in the pyrites burners of a sulphuric acid plant in order to utilise the sulphur dioxide for the production of sulphuric acid. Care must be taken to regulate the air supply and temperature so as to prevent the formation of zinc sulphate from the blende, as this is reduced with difficulty.

(*b*) *Reduction and Distillation.*—The reduction is represented by the equation

$$ZnO + C = Zn + CO.$$

In order to effect the reduction the roasted ore is mixed with about half its weight of powdered coke or anthracite and a little salt and heated in fireclay retorts, which are about 5 feet long, of an elliptical section (11″ × 7½″), and arranged in double rows, often to the number of 150 on each side, in a furnace, fired by producer gas, with a complete system of regenerative heating (Fig. 282).

A clay condenser is luted on to the front of the retort and serves to

condense the zinc: the length of the condenser is designed to maintain a temperature at which the zinc condenses as a liquid, since if solid particles of ZINC DUST are formed (as may happen on a cold or windy night) they refuse to coalesce and must be recovered by redistillation. The carbon monoxide burns at the mouth of the condenser with a flame which is coloured yellow by the slow vaporisation of salt; if the flame is coloured green by burning zinc-vapour a sheet iron "prolong" is added to complete the condensation. The distillation covers a period

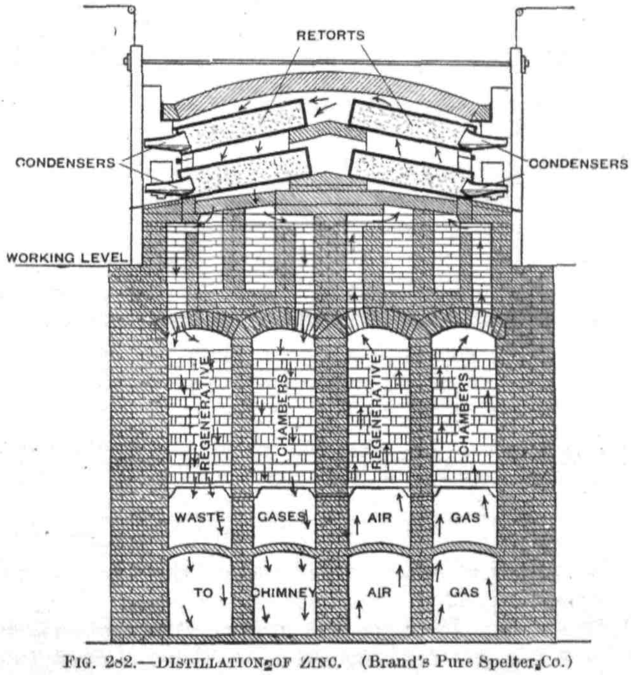


FIG. 282.—DISTILLATION OF ZINC. (Brand's Pure Spelter Co.)

Two sets of flues are provided, as shown at the bottom of the figure, to deliver air and gas through heated brickwork to the centre and end of the furnace; the waste gases pass through a duplicate mass of brickwork and pairs of flues to the chimney. Regenerative heating is effected by reversing the direction of the gases every twenty minutes; this also serves to equalise the temperatures of the retorts on the two sides of the furnace. Notice that two-thirds of the furnace is below the ground-level.

of twenty-four hours between successive charges, and during this time the condensed zinc is raked out once or twice from the condenser into iron pots and cast into moulds. The temperature of distillation is about 1400° and the recovery of zinc is about 75 per cent. Any cadmium that may be present in the ore comes over with the first portions of the distillate, and most of the lead is also carried over as metal.

(c) *Refining.*—Crude zinc or SPELTER contains about 98 per cent. of zinc. The principal impurities are lead (especially when made from

sulphide ores containing galena), cadmium, iron, arsenic, and carbon. Redistillation would not purify the metal sufficiently, since the cadmium and arsenic, and even the lead, are volatile, and would pass over with the zinc. Any large excess of lead may be removed by melting the metal in a hearth with a well in it, in which the greater part of the lead separates out by liquation; the upper layer of zinc (containing only about 1 per cent. of lead) is ladled off and remelted with a little nitre, which oxidises the remaining lead and other impurities which rise to the surface as a scum. Zinc can be freed from arsenic by adding sodium and heating for several hours; this process probably involves the formation of an arsenate. Very pure commercial zinc is obtained by electrolysis.

Extraction of Zinc by Electrolysis.

Electrolytic processes of extracting zinc are employed in certain cases. Thus, an ingenious method of working up the Broken Hill ores was based on the following series of operations.

(*a*) *Chlorination.*—The mineral sulphides were converted by the action of chlorine into a bath of molten chlorides, from which the rock or "gangue" could be separated easily.

$$ZnS + Cl_2 = ZnCl_2 + S$$
$$PbS + Cl_2 = PbCl_2 + S$$
$$Ag_2S + Cl_2 = 2AgCl + S.$$

(*b*) *Precipitation.*—The silver was precipitated by the addition of lead, and the lead by the addition of zinc.

$$2AgCl + Pb = PbCl_2 + 2Ag$$
$$PbCl_2 + Zn = ZnCl_2 + Pb.$$

In this way the whole of the silver and the whole of the lead were recovered.

(*c*) *Electrolysis.*—By electrolysis of the molten zinc chloride, the zinc was separated and the whole of the chlorine recovered for use again as in (*a*).

$$ZnCl_2 = Zn + Cl_2.$$

This method was only partially successful because a wet process was required to remove iron and manganese before electrolysis. The electrolysis of zinc chloride, prepared by double decomposition from zinc oxide and calcium chloride in presence of carbon dioxide,

$$ZnO + CO_2 + CaCl_2 = ZnCl_2 + CaCO_3,$$

has, however, been proposed as a method of utilising the calcium chloride formed as a waste product in the Solvay process, and in particular of recovering the chlorine which it contains.

In a more recent process zinc sulphide is roasted in such a way as to give a maximum yield of sulphate, and the remainder of the oxidised

ore is converted into sulphate by the action of sulphuric acid. The solution of zinc sulphate is freed from all nobler metals, *e.g.*, cadmium, cobalt, nickel, copper, silver, etc., by contact with zinc powder, and is then electrolysed so as to give a deposit of pure zinc (99·5 % Zn) on an aluminium cathode, whilst sulphuric acid is regenerated at a lead anode. Special care is needed to remove the last traces of nickel and cobalt, since a few parts per million of either metal are sufficient to prevent the formation of a uniform deposit of zinc.

Properties of Metallic Zinc.

(*a*) *Physical Properties.*—Zinc is a white metal, of density 7·1, as compared with 7·8 for iron; it melts at 419° and boils at 918°. The metal is trimorphous (like iron), undergoing changes of crystalline form at 170° and at 340°. Commercial zinc is brittle at the temperature of the air, but malleable at about 120°, at which temperature it can be rolled into sheets and drawn into wire; at 200° it again becomes very brittle and can be powdered in a mortar. Highly purified zinc, on the other hand, does not show this behaviour and is malleable at all temperatures.

(*b*) *Chemical Properties.*—Commercial zinc dissolves rapidly in dilute acids. The purity of zinc may, indeed, be gauged roughly by the rate at which it dissolves in dilute sulphuric acid, highly purified zinc hardly dissolving at all, whilst ordinary zinc rapidly liberates hydrogen freely,

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Zinc also dissolves in dilute hydrochloric acid, forming zinc chloride and hydrogen, whilst with dilute nitric acid it gives a mixture of nitric oxide, nitrous oxide, and ammonia, in different proportions according to the conditions.

Zinc does not oxidise in purified air at atmospheric temperatures, but it is attacked slowly by moist air containing carbon dioxide, a white film of carbonate or oxide being formed. It is, however, less readily corroded than iron, since the carbon dioxide is retained and not set free again by oxidation (see the rusting of iron, p. 779); zinc is therefore used to protect that metal from atmospheric corrosion or rusting. GALVANISED IRON is sheet-steel coated with a thin layer of zinc by immersing it, after thoroughly cleaning its surface, in a bath of the molten zinc; unlike tinned iron, which is only effective when the film of tin is complete, zinc diverts to itself the attack of the carbonic acid and protects the iron even when the film of metal is scratched or partly worn away.

When zinc is heated strongly in air it ignites and burns with a greenish-white flame, forming **zinc oxide**, ZnO,

$$2Zn + O_2 = 2ZnO.$$

It combines directly with chlorine, forming **zinc chloride**, $ZnCl_2$, but

does not combine directly with hydrogen, nitrogen, or carbon. **Zinc methyl,** $Zn(CH_3)_2$, a compound which may be compared with calcium hydride, CaH_2, can, however, be prepared by the action of zinc on methyl iodide,

$$2Zn + 2CH_3I = Zn(CH_3)_2 + ZnI_2,$$

and a **zinc nitride,** Zn_3N_2, corresponding with magnesium nitride, Mg_3N_2, has been prepared by heating zinc in a current of ammonia,

$$3Zn + 2NH_3 = Zn_3N_2 + 3H_2.$$

Zinc differs from magnesium, but resembles aluminium in dissolving in solutions of alkali hydroxides, liberating hydrogen and forming a solution of an alkali zincate,

$$Zn + 2NaOH = \underset{\text{Sodium zincate}}{Zn(ONa)_2} + H_2.$$

(c) *Uses of Zinc.*—The principal uses of zinc are for galvanising iron and for alloying with copper to make brass (p. 833) and similar alloys. Zinc oxide is used as a paint, under the name of ZINC WHITE, and precipitated zinc sulphide, combined with precipitated barium sulphate, is used as a paint under the name of lithopone (p. 647). Zinc chloride is used to clean metals before soldering and in various industries.

Compounds of Zinc.

Zinc Chloride, $ZnCl_2$.

Anhydrous zinc chloride is obtained by passing chlorine over heated metallic zinc, or by the action of chlorine on zinc blende (p. 870),

$$ZnS + Cl_2 = ZnCl_2 + S.$$

An earlier method of preparation was by heating anhydrous zinc sulphate with sodium chloride or calcium chloride,

$$ZnSO_4 + 2NaCl = ZnCl_2 + Na_2SO_4;$$

the crude zinc chloride which distils solidifies in the receiver to a soft waxy mass known as BUTTER OF ZINC.

A solution of zinc chloride is obtained by dissolving zinc or its oxide or carbonate in hydrochloric acid, or by the action of calcium chloride and carbon dioxide on zinc oxide,

$$ZnO + CaCl_2 + CO_2 = ZnCl_2 + CaCO_3.$$

When aqueous solutions of zinc chloride are concentrated, hydrogen chloride is lost, and precipitates are formed which consist of mixtures in different proportions of the oxychloride, HO·ZnCl, and the hydroxide, $Zn(OH)_2$,

$$ZnCl_2 + H_2O = HO{\cdot}ZnCl + HCl$$
$$HO{\cdot}ZnCl + H_2O = Zn(OH)_2 + HCl;$$

the water can, however, be removed by evaporation under reduced

pressure or by electrolysing with a cheap carbon anode so long as oxygen is evolved, and then using good graphite electrodes for the subsequent separation of zinc and chlorine from the anhydrous salt. By concentrating the aqueous solution, after adding a little concentrated hydrochloric acid to the liquor to prevent hydrolysis, deliquescent crystals of the **monohydrate,** $ZnCl_2,H_2O$, can be prepared.

Zinc chloride is a soluble, deliquescent salt, which melts at 365° when pure, but at temperatures down to 100° when impure, and is commonly cast into sticks for use in the laboratory. It boils at 730°.

Zinc chloride is used in surgery as a caustic. A concentrated solution of zinc chloride dissolves cellulose (cotton) and was formerly used in preparing carbon filaments for incandescent lamps and in the preparation of "artificial silk." It is also used for preserving wood. Zinc chloride, prepared by the action of zinc on commercial "spirits of salts," is used by plumbers under the name of "killed spirits" for cleaning metals before soldering. In organic chemistry, zinc chloride is used, like sulphuric acid, as a dehydrating agent and as a catalyst for the removal of water or of hydrogen chloride.

Zinc Oxide and Hydroxide.

Zinc oxide, ZnO, is manufactured on a large scale by distilling zinc in a current of air or steam; this form of the oxide is used as a paint under the name of ZINC WHITE. Although white at ordinary temperatures, zinc oxide becomes yellow when heated.

Zinc oxide is also made, for use in pharmacy, by precipitating a solution of zinc sulphate with sodium carbonate, and washing, collecting, and igniting the precipitated carbonate.

The oxide, when mixed with a solution of zinc chloride, sets to a hard mass of zinc oxychloride,

$$ZnO + ZnCl_2 + H_2O = 2Zn(OH)Cl;$$

with aqueous phosphoric acid it sets to a hard zinc oxyphosphate which is still used extensively as a cement in dentistry.

Zinc hydroxide, $Zn(OH)_2$, an amphoteric compound, possessing both basic and acid properties (p. 529), is precipitated by adding sodium hydroxide to a solution of a zinc salt, care being taken to avoid an excess of the alkali, which redissolves the hydroxide, forming a ZINCATE (p. 872). Zinc hydroxide, like magnesium hydroxide, is soluble in a solution of ammonium chloride; it is also soluble in an excess of ammonia.

Zinc Carbonates.

Normal zinc carbonate, $ZnCO_3$, occurs naturally as the mineral CALAMINE or SMITHSONITE.

When sodium carbonate is added to a solution of a zinc salt, a **hydrated carbonate,** $ZnCO_3,H_2O$, can be obtained under certain conditions; this is probably a **hydroxycarbonate,** $HO{\cdot}Zn{\cdot}CO_3H$ (compare

magnesium hydroxycarbonate, p. 618). Basic carbonates are, however, generally obtained, especially on warming (compare magnesium); these are probably mixtures of the hydroxycarbonate with zinc hydroxide in different proportions.

Zinc Sulphide and Sulphate.

Zinc sulphide, ZnS, occurs naturally as BLENDE, in mineral veins, in which it is commonly associated with galena and with some crystalline vein-mineral such as quartz, calcite, fluorspar, or barytes. Although pure zinc sulphide is white, the mineral is generally dark in colour, often nearly black, owing to the presence of sulphides of other metals, and especially of iron.

Zinc sulphide can be prepared by igniting a mixture of finely powdered sulphur and zinc dust, which is very combustible and often explosive; it is also obtained by heating zinc oxide or zinc carbonate with sulphur. The rapid precipitation of zinc sulphide by adding ammonium sulphide to a solution of a zinc salt, or by passing hydrogen sulphide through a solution of zinc acetate, yields a gelatinous product; slow precipitation, however, yields a crystalline product having the composition of a **monohydrate,** ZnS,H_2O.

Natural crystals of blende are phosphorescent, and the precipitated sulphide can be rendered phosphorescent by heating it to a white heat in a covered crucible (Sidot's blende). Pure zinc sulphide is not phosphorescent, the phosphorescence being apparently due to the presence of traces of impurities, especially bismuth sulphide. Crystals of zinc sulphide are also used, *e.g.*, in the SPINTHARISCOPE, to detect the α-particles or helium atoms expelled from radioactive elements during disintegration; each particle or atom produces a visible flash on the surface of the crystal.

Zinc sulphide dissolves readily in dilute mineral acids, but is insoluble in acetic acid.

Zinc sulphide is used as a white paint, especially in France, where paints containing lead are not allowed (see "lithopone," p. 647 above).

Zinc sulphate, $ZnSO_4,7H_2O$, formerly known as WHITE VITRIOL, is obtained by dissolving zinc in dilute sulphuric acid, or by roasting blende and extracting with water. It crystallises from water in well-formed prisms and forms double salts such as $K_2SO_4,ZnSO_4,6H_2O$, which are isomorphous with the corresponding salts of magnesium and other bivalent metals. When heated strongly it loses sulphur dioxide and oxygen and leaves finally zinc oxide.

Zinc sulphate is used in medicine and as a preservative of wood and hides.

Zinc Nitrate, $Zn(NO_3)_2$.

This salt, prepared by the action of nitric acid on the oxide, carbonate, or sulphide, usually crystallises from water as the **hexahydrate,**

$Zn(NO_3)_2,6H_2O$, a colourless, deliquescent salt, which melts completely when heated to 36·4° (Fig. 283). Below −17° it crystallises with $9H_2O$. A trihydrate crystallises from concentrated solutions, but melts at 45·5°. The salt loses oxides of nitrogen when heated, and leaves a residue of basic nitrate.

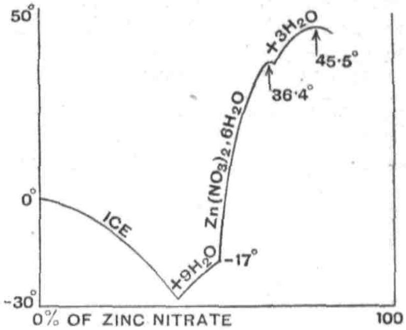


FIG. 283.—HYDRATES OF ZINC NITRATE.

Detection and Estimation of Zinc.

When heated in the Bunsen flame with cobalt nitrate, compounds of zinc give a bright green mass. Ammonium sulphide precipitates the white **sulphide,** ZnS, which is soluble in dilute acids. The alkali carbonates give a white precipitate of "basic carbonate" which is partly soluble in alkalies and in ammonium chloride. Potassium cyanide gives a white precipitate of **zinc cyanide,** ZnC_2N_2, which dissolves in an excess of the reagent as $K_2ZnC_4N_4$ (compare nickel, p. 807, and copper, p. 840).

Zinc is estimated quantitatively by precipitating as a carbonate, by boiling with aqueous sodium carbonate; the product is collected, ignited, and weighed as **zinc oxide,** ZnO. Other metals which give insoluble carbonates under the same conditions must be eliminated. Another method consists in precipitating the zinc as **zinc sulphide,** ZnS, by adding ammonium sulphide in presence of ammonia and ammonium chloride, and washing, drying, and weighing the precipitate.

Several volumetric methods are in use, the principal of which makes use of titration with sodium sulphide. Zinc can also be titrated against a ferrocyanide, using uranium acetate as an indicator. Zinc is estimated electrolytically by precipitating the metal by an electric current in a platinum crucible.

The atomic weight of zinc is based mainly on exact determinations of the ratios $ZnBr_2 : 2Ag$ and $ZnBr_2 : 2AgBr$.

48. CADMIUM. Cd = 112·4.

Occurrence.

Cadmium nearly always accompanies zinc in its ores, in amounts varying from 1 to 5 per cent. **Cadmium sulphide,** CdS, occurs alone only rarely, in Scotland, Bohemia, and Pennsylvania, as GREENOCKITE.

Metallic Cadmium.

(*a*) *Preparation.*—Cadmium is obtained in the first stages of the smelting of zinc, since its oxide is more easily reduced by carbon than

zinc oxide and the metal is more volatile than zinc. The first portion of the vapour therefore burns with a brown flame (brown blaze) due to the cadmium. The metal can be extracted by redistilling, with coal, the first portion of the dust which condenses in the iron condensers used in the distillation of zinc.

Considerable quantities of cadmium are now extracted from the zinc sulphate used in the manufacture of lithopone. This is purified by adding zinc to the solution, which throws down a mud containing 30 to 70 per cent. of cadmium as well as other impurities such as copper, lead, and arsenic; the mud is dried and cast into plates, these plates being used as anodes in an electrolytic bath of cadmium sulphate from which metallic cadmium is deposited.

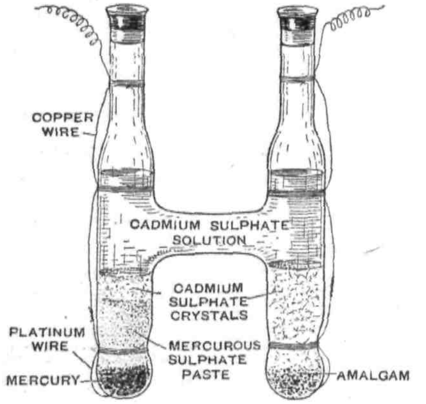


FIG. 284.—WESTON CADMIUM CELL.

(*b*) *Properties.*—Cadmium is a metal with a tin-white colour and is easily obtained in a crystalline form by subliming it in a current of hydrogen. It is intermediate in properties between zinc and mercury; thus, its density is 8·6, its melting-point is 321°, and it boils at 778°.

Its principal use is in preparing FUSIBLE ALLOYS, containing lead, tin, bismuth, and cadmium; some of these quaternary alloys melt as low as 65°. A "Clark cell" with the zinc replaced by cadmium is commonly used under the name of the WESTON CELL or CADMIUM CELL (Fig. 284) as a secondary standard of electromotive force; it has the advantage of a smaller temperature-coefficient than the Clark cell, and its *E.M.F.* approximates more nearly to 1 volt.

Compounds of Cadmium.

Cadmium chloride, $CdCl_2$, is obtained by heating the metal or oxide in a current of dry chlorine, and sublimes in pearly leaflets; it melts at 560° and boils at about 900° as compared with 365° and 730° for zinc chloride, and is deliquescent. The **dihydrate,** $CdCl_2,2H_2O$, is easily prepared by dissolving the metal, oxide, or carbonate in hydrochloric acid and concentrating the solution; it is very soluble in water and deliquescent. Cadmium chloride is more stable than the chlorides of zinc and magnesium, and, unlike them, is not decomposed when its aqueous solution is boiled or concentrated.

Cadmium oxide, CdO, is prepared, like zinc oxide, by burning the metal, and forms a brown powder.

Cadmium hydroxide, $Cd(OH)_2$, is precipitated as a white powder on adding sodium or potassium hydroxide to a solution of a cadmium salt; like magnesium hydroxide, it is insoluble in alkali hydroxides and differs in this respect from zinc hydroxide, but, like the latter, it dissolves readily in ammonium hydroxide.

Cadmium carbonate, $CdCO_3$, is sometimes present in crystals of calamine, $ZnCO_3$, to which it imparts a yellow colour. On precipitating a solution of a cadmium salt with a carbonate a mixture of the carbonate and hydroxide is obtained, as in the case of magnesium and zinc.

Cadmium sulphide, CdS, is obtained as a fine yellow precipitate on passing hydrogen sulphide through a solution of a cadmium salt; it does not dissolve in dilute hydrochloric acid, differing in this respect from zinc sulphide, but it dissolves in boiling dilute nitric or sulphuric acid and in concentrated hydrochloric acid, the action shown in the equation

$$CdS + 2HCl \rightleftharpoons CdCl_2 + H_2S$$

being reversible. Cadmium sulphide is used as a yellow pigment.

Cadmium sulphate, prepared by dissolving the oxide or carbonate in sulphuric acid, crystallises as the hydrate, $3CdSO_4,8H_2O$, and is used in this form to saturate the electrolyte in the Weston cell.

Detection and Estimation of Cadmium.

Cadmium differs from Mg, Ca, Sr, Ba, and Zn in giving a **sulphide** which is insoluble in dilute hydrochloric acid; it is therefore thrown down as a yellow precipitate from acid solutions by the action of hydrogen sulphide. In separating it from mercury and other metals which give insoluble sulphides in acid solution, advantage is taken of the fact that cadmium sulphide dissolves in nitric acid (unlike mercury sulphide) and in dilute sulphuric acid (unlike copper sulphide). Use is also made of the fact that cadmium hydroxide (unlike bismuth hydroxide) is soluble in ammonia. Cadmium sulphide differs from the yellow sulphides of arsenic, antimony, and tin in being insoluble in boiling potassium hydroxide or in ammonium sulphide, which dissolve these sulphides very easily.

Cadmium is generally estimated by precipitating it as carbonate by means of an alkaline carbonate, washing, igniting, and weighing as **cadmium oxide.** It is also estimated as the **sulphide,** CdS, which is dried at 100°.

Its atomic weight is based upon direct determinations of the ratio Cd : CdO.

80. Mercury. Hg = 200·0.

Occurrence.

Mercury occurs very sparingly in the free state, and is practically all extracted from **mercuric sulphide** or CINNABAR, HgS. This is found at Almaden in Spain, in Austria (Idria), Italy, and California.

The Almaden mine in Spain, which has been worked since 415 B.C., is still the chief producer. This mine includes three vertical veins, about 600 feet long and 12 to 15 feet thick, increasing in richness as the depth increases; the vein mineral is sandstone or quartzite, SiO_2, containing about 8 per cent. of HgS.

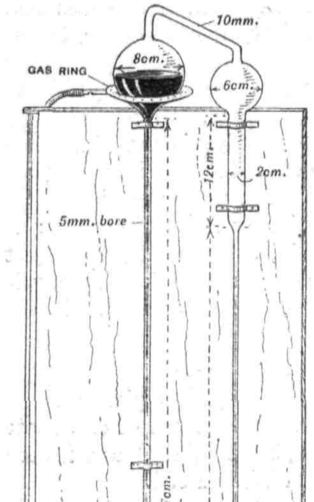


FIG. 285.—APPARATUS FOR PURIFYING MERCURY BY DISTILLATION.

Preparation of Metallic Mercury.

The extraction of mercury depends on the instability of its oxide; thus, when an ore containing mercury sulphide is heated in a stream of air, it gives, not the oxide (as in the case of zinc and cadmium), but the free metal,

$$HgS + O_2 = Hg + SO_2.$$

The mercury distils off and is condensed either by air or by water.

The ore is not mixed with fuel, but is heated either by the flame from a hearth or by producer gas (p. 467), and air is drawn through it at a sufficient rate to prevent mercury sulphide from volatilising without undergoing decomposition. The process is remarkable in that ores containing as little as 0·2 per cent. can be used without concentration.

In order to avoid the loss of mercury, carried away as vapour by the current of air in the preceding process, the richer ores are distilled in retorts with lime or with iron,

$$4HgS + 4CaO = 4Hg + 3CaS + CaSO_4$$
$$HgS + Fe = Hg + FeS.$$

Purification of Mercury.

Crude mercury is purified by distillation in an iron retort with a little chalk or iron to decompose any compounds of mercury, and by filtering it through wash leather. In the laboratory it can be freed from baser metals such as copper, lead, zinc, and bismuth, by being dropped in the form of small globules through dilute nitric acid of density 1·1; it can also be purified by being made the anode in an electrolytic

cell, when the baser metals pass into solution before the mercury. The most effective method of purification, however, is by continuous distillation in a vacuum in an apparatus arranged so that the distilled mercury acts as a barometric column (Fig. 285).

Properties and Uses of Metallic Mercury.

(*a*) *Physical Properties.*—Pure mercury is a silvery liquid having a density of 13·595 at 0°, and is the heaviest liquid known at atmospheric temperatures. It freezes at — 38·85°, and boils at 357·25°; the vapour density shows that the metal is monatomic, like zinc and cadmium. When pure, it does not change in air or in oxygen, but when it contains traces of impurities (foreign metals such as zinc or lead) it absorbs oxygen and becomes coated with a grey film; such mercury leaves a "tail" when allowed to run over a porcelain or glass surface. A column of mercury 106·3 cm. long and 1 sq. mm. in cross-section (or weighing 14·4521 grams) at 0° has, by definition, a resistance of 1 ohm.

(*b*) *Valency.*—Mercury differs from zinc and cadmium in forming two important series of compounds, namely, univalent MERCUROUS COMPOUNDS in which the equivalent of the metal is 200, and bivalent MERCURIC COMPOUNDS in which it is only 100; in this respect mercury shows a striking relationship to copper. The vapour of mercurous chloride is, however, represented by the formula Hg_2Cl_2, and may therefore contain bivalent atoms of mercury as shown in the formula Cl·Hg·Hg·Cl. On the other hand, in mercury vapour, the valency appears to be reduced to zero, since the atoms of mercury refuse to combine with one another.

A comparison of the cuprous and cupric salts with the mercurous and mercuric salts reveals a marked tendency in each case for the -*ous* salts to break down into metal and an -*ic* salt, as, for instance, when cuprous oxide is dissolved in sulphuric acid,

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O,$$

or when mercurous chloride is acted on by ammonia,

$$Hg_2Cl_2 + 2NH_3 = (NH_2Hg)Cl + NH_4Cl + Hg;$$

a contrast between the two metals is found in the fact that mercurous chloride breaks down when heated into mercuric chloride and mercury,

$$Hg_2Cl_2 = HgCl_2 + Hg,$$

whereas cupric chloride, on the contrary, breaks down into cuprous chloride and chlorine,

$$2CuCl_2 = Cu_2Cl_2 + Cl_2.$$

Again, cupric iodide is too unstable to persist even at atmospheric temperatures, and cuprous nitrate is still unknown, whereas the corresponding salts of mercury are quite stable; on the other hand,

mercurous sulphide is not known, although cuprous sulphide, Cu_2S, is readily prepared. These points of similarity and of contrast are set out below.

Cuprous compounds	Cu_2O	Cu_2S	Cu_2Cl_2	Cu_2I_2	—	$[Cu_2SO_4]$
Cupric ,,	CuO	CuS	$CuCl_2$	—	$Cu(NO_3)_2$	$CuSO_4$
Mercurous ,,	Hg_2O	—	Hg_2Cl_2	Hg_2I_2	$HgNO_3$	Hg_2SO_4
Mercuric ,,	HgO	HgS	$HgCl_2$	HgI_2	$Hg(NO_3)_2$	$HgSO_4$

(*c*) *Chemical Properties.*—When heated in air or oxygen below its boiling-point, mercury absorbs oxygen, forming red **mercuric oxide,**

$$2Hg + O_2 = 2HgO.$$

At a slightly higher temperature (below 500°) this oxide decomposes again into its constituents,

$$2HgO = 2Hg + O_2.$$

Hydrochloric acid has little action on mercury, but hot concentrated sulphuric acid dissolves it, giving **mercuric sulphate** and sulphur dioxide,

$$Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O.$$

Nitric acid dissolves it readily, giving oxides of nitrogen and **mercurous nitrite,** $HgNO_2$, from which by the further action of nitric acid, **mercurous nitrate,** $HgNO_3$, various basic salts and finally **mercuric nitrate,** $Hg(NO_3)_2$, are formed. In the same way, iodine in excess gives red **mercuric iodide,** HgI_2, but with excess of mercury a green **mercurous iodide,** Hg_2I_2, is formed.

(*d*) *Amalgams.*—Mercury dissolves many metals, forming AMALGAMS. It does not dissolve the metals of the iron group, and is therefore commonly packed in iron bottles or flasks, each holding 76½ lb. of the metal. From some amalgams crystalline compounds have been obtained; *e.g.*, sodium gives a series of compounds, $NaHg_4$, $NaHg_2$, $NaHg$, etc., of which the most important has the formula $NaHg_2$ and melts at 360°; the corresponding potassium-compound melts at 279°. The plastic amalgam of TIN is used in coating mirrors, and SODIUM AMALGAM is often used in place of sodium as a reducing agent. AMALGAMATED ZINC is used in electric batteries, as it is less readily attacked, when the circuit is open, than commercial zinc. COPPER AMALGAM containing about 25 to 33 per cent. of copper was used formerly in dentistry for stopping teeth; it becomes plastic when rubbed in a mortar and subsequently sets to a hard mass without change of volume. The DENTAL ALLOY now used in making DENTAL AMALGAM contains the compound Ag_3Sn and sets as a result of the chemical change shown in the equation

$$Ag_3Sn + 4Hg = Ag_3Hg_4 + Sn.$$

(*e*) *Uses.*—The largest quantities of mercury are used in the extraction of silver and gold; other uses are the manufacture of

mercury fulminate for detonators, of mercurial drugs, and in the construction of physical apparatus (barometers, thermometers, vacuum pumps, etc.), where a liquid of high density, good thermal conductivity, or low vapour-pressure is required.

Mercurous Compounds.

Mercurous chloride, or CALOMEL, Hg_2Cl_2, is obtained by heating an intimate mixture of mercuric chloride and mercury, when calomel sublimes,

$$HgCl_2 + Hg = Hg_2Cl_2.$$

Another method consists in subliming a mixture of mercuric sulphate, mercury, and common salt,

$$HgSO_4 + Hg + 2NaCl = Hg_2Cl_2 + Na_2SO_4.$$

In both cases the sublimate obtained must be washed thoroughly with water to remove any mercuric chloride which may have sublimed with it.

Mercurous chloride is a white powder which is almost insoluble in water, about 4 mg. per litre at 20°, as compared with 1·5 mg. of silver chloride. When heated it volatilises without melting. Under ordinary conditions, the vapour will amalgamate gold-leaf, and the vapour density shows that the mercurous chloride has dissociated into a mixture of mercuric chloride and mercury,

$$Hg_2Cl_2 = Hg + HgCl_2.$$

When, however, the mercurous chloride has been dried carefully and all precautions are taken to exclude traces of moisture, the mercurous chloride volatilises as such, and the vapour density corresponds with the formula Hg_2Cl_2. Still further drying appears to prevent the compound from vaporising at the usual temperature.

Calomel is decomposed when heated with sodium or potassium hydroxide,

$$2Hg_2Cl_2 + 4KOH = 4KCl + 4Hg + O_2 + 2H_2O.$$

When ammonia is added, it turns black, owing apparently to the formation of "infusible white precipitate," NH_2HgCl (p. 883), and mercury,

$$Hg_2Cl_2 + 2NH_3 = NH_2HgCl + NH_4Cl + Hg;$$

the "infusible precipitate" is colourless and the black colour of the product is due to tiny globules of mercury. A product obtained by the action of gaseous ammonia on calomel, and formerly regarded as $Hg_2Cl_2,2NH_3$, is probably a similar mixture of "fusible white precipitate," of the empirical composition $HgCl_2,2NH_3$ (see below, p. 883), with metallic mercury.

Calomel is used in medicine as a purgative and, unlike mercuric chloride (corrosive sublimate), is not poisonous in moderate doses.

Mercurous oxide, Hg_2O, or "grey oxide" of mercury, is precipitated as a blackish-brown powder on adding a solution of a caustic alkali to a solution of a mercurous salt, *e.g.*,

$$2HgNO_3 + 2KOH = Hg_2O + H_2O + 2KNO_3.$$

It is decomposed by light as follows:

$$Hg_2O = Hg + HgO,$$

but when heated at 100° it combines with oxygen to form the red oxide.

Mercurous sulphide is not known; when a mercurous salt is precipitated with hydrogen sulphide, a mixture of mercuric sulphide and mercury is obtained.

Mercurous sulphate, Hg_2SO_4, is obtained by heating concentrated sulphuric acid with an excess of mercury; it is easily soluble in the hot concentrated acid, but sparingly so in water, and is precipitated as a white powder on diluting the acid solution. It is decomposed by water, giving mercury, mercuric sulphate, and a basic sulphate, $3HgO,SO_3$.

Mercurous nitrite, $HgNO_2$, the first product of the action of nitric acid on mercury, separates in bright yellow crystals when mercury is covered with dilute nitric acid, *e.g.*, with acid of density 1·11 at 35° during 50 hours. Hot water decomposes it partially into mercuric nitrite and mercury,

$$2HgNO_2 = Hg(NO_2)_2 + Hg,$$

and slightly stronger acid converts it into mercurous nitrate.

Mercurous nitrate, $HgNO_3$, is obtained by the action on mercury of cold dilute nitric acid of density 1·14 (hot concentrated nitric acid gives mercuric nitrate). It crystallises as the **dihydrate,** $HgNO_3,2H_2O$, but is decomposed by an excess of water, forming basic nitrates, the composition of which depends upon the conditions. In presence of sulphuric acid, mercury reduces nitric acid quantitatively to nitric oxide,

$$6Hg + 3H_2SO_4 + 2HNO_3 = 3Hg_2SO_4 + 2NO + 4H_2O;$$

this reaction is used in the LUNGE NITROMETER (p. 396) to estimate nitric acid.

Mercurous carbonate, Hg_2CO_3, is precipitated on adding potassium hydrogen carbonate to a solution of mercurous nitrate; it is a yellow powder which is decomposed at 130°, thus:

$$Hg_2CO_3 = Hg + HgO + CO_2.$$

MERCURIC COMPOUNDS.

Mercuric chloride, or CORROSIVE SUBLIMATE, $HgCl_2$, is prepared by heating mercury in chlorine gas, or by heating a dry mixture of

common salt and mercuric sulphate, a little manganese dioxide being added as an oxidising agent to prevent the formation of calomel,

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

Mercuric chloride sublimes in needles which have a high density (5·4; Hg_2Cl_2 = 7·1). It melts at 277° and boils at 303°. It is far more soluble in hot than in cold water, in which it is somewhat sparingly soluble; thus a solution saturated at 100° contains 35 per cent. of $HgCl_2$, whilst one saturated at 0° contains only 4 per cent. It is remarkable in being easily soluble in alcohol and in ether, in the latter more so than in water. The aqueous solution is remarkable in that it is not an electrolyte and will not conduct an electric current.

It is a powerful poison, but is used largely in medicine; in surgery it is used as an antiseptic. It is also used industrially as a preservative for skins and furs and for preserving wood.

Mercuric chloride absorbs ammonia gas, forming the compound $HgCl_2,NH_3$, which can be distilled without decomposition. It combines with other chlorides to form crystalline double chlorides, such as

$$KCl,HgCl_2,H_2O \quad \text{or} \quad KHgCl_3,H_2O$$
$$NaCl,HgCl_2,2H_2O \quad \text{or} \quad NaHgCl_3,2H_2O$$
$$2NH_4Cl,HgCl_2,H_2O \quad \text{or} \quad (NH_4)_2HgCl_4,H_2O.$$

These double salts are more easily soluble in water than mercuric chloride. The compound, $3HgCl_2,2PCl_5$, formed by the combination of mercuric chloride and phosphorus pentachloride, forms glistening needles and can be sublimed.

On adding aqueous ammonia to a solution of mercuric chloride, the INFUSIBLE WHITE PRECIPITATE of pharmacy is obtained; this has the composition NH_2HgCl, and is formed as follows:

$$2NH_3 + HgCl_2 = NH_2HgCl + NH_4Cl.$$

It was formerly regarded as an aminomercuric chloride, $NH_2{\cdot}HgCl$, in which one chlorine atom of mercuric chloride has been replaced by the amino-group NH_2; alternatively it may be regarded as a mercuriammonium chloride, $(NH_2Hg)Cl$, in which two atoms of hydrogen have been replaced by an atom of bivalent mercury, or better as a double salt, NHg_2Cl,NH_4Cl, of the dimercuriammonium chloride, NHg_2Cl, into which it is converted by boiling with water.

The FUSIBLE WHITE PRECIPITATE of pharmacy is obtained by adding a solution of mercuric chloride to a hot solution of ammonium chloride and ammonia, so long as the precipitate which is formed dissolves. The crystals which separate on cooling have the composition $HgCl_2,2NH_3$. This compound is perhaps a substituted ammonium chloride, $Hg\langle{NH_3Cl \atop NH_3Cl}$, but may also be regarded, like the

"infusible" compound, as a double salt, $NHg_2Cl,3NH_4Cl$, of the dimercuriammonium chloride, NHg_2Cl, since this is again produced by boiling the "fusible precipitate" with water.

Dimercuriammonium chloride, NHg_2Cl, prepared by boiling either of the preceding compounds with water, is a yellow powder which is not decomposed by boiling water, and is only very slightly soluble in cold dilute hydrochloric acid, but cold potassium hydroxide liberates the explosive **oxide,** $(NHg_2)_2O$. When heated at 300° it decomposes into mercury, calomel, and nitrogen,

$$2NHg_2Cl = N_2 + 2Hg + Hg_2Cl_2.$$

Mercuric iodide, HgI_2, is precipitated on adding a solution of potassium iodide to a solution of mercuric chloride; when it first separates it is yellow in colour, but quickly becomes red. When the change is observed under the microscope it is seen that the yellow form consists of plates (orthorhombic system) which change into scarlet octahedra (tetragonal system). Mercuric iodide is in fact dimorphous with a well-defined transition-temperature at 126°. When the scarlet form is heated above 126° it changes into the yellow form, which is stable above this temperature. The yellow crystals change gradually into the scarlet form on standing at the ordinary temperature; this change is accelerated by scratching or rubbing, a line of scarlet appearing where the crystals are touched. When the iodide is sublimed, the vapour usually condenses in the form of yellow crystals, but a colourless snow may appear as a transitory form when the vapour of the iodide is admitted suddenly to an exhausted receiver.

Mercuric iodide dissolves readily in an excess of potassium iodide, forming a solution from which the double salt **potassium mercuri-iodide,** $2KI,HgI_2$ or K_2HgI_4, can be crystallised. This salt is not decomposed by potassium hydroxide, although the mercury can be precipitated by hydrogen sulphide. The solution obtained by adding potassium hydroxide to the double salt is known as NESSLER'S REAGENT and forms a very delicate test for traces of ammonia, which produce a yellow to brown coloration or a brown precipitate (p. 886).

Mercuric cyanide, HgC_2N_2, was prepared by Scheele by the action of mercuric chloride or oxide on Prussian blue, and is still prepared by the latter process. It can also be prepared by dissolving mercuric oxide in prussic acid, or in potassium cyanide. It dissolves in 8 parts of cold water or in 2 parts of boiling water, and crystallises from water in colourless needles, but differs from the chloride in being insoluble in absolute alcohol. When heated it decomposes into mercury and cyanogen,

$$HgC_2N_2 = Hg + C_2N_2.$$

Mercuric cyanide is remarkable for the fact that it behaves more like an organic compound or a co-ordinated compound such as

$K_4FeC_6N_6$, than a simple salt, *e.g.*, its aqueous solution has an extremely low electrolytic conductivity, is not precipitated by sodium hydroxide or by potassium iodide, and only liberates hydrogen cyanide slowly when boiled with dilute acids; it is, however, decomposed by sulphuretted hydrogen.

Mercuric thiocyanate, $Hg(CNS)_2$, prepared by precipitation from mercuric chloride and ammonium thiocyanate, is used in the preparation of "Pharaoh's serpents," since it swells up and leaves a very bulky carbonaceous ash when it burns. **Mercuric cyanate,** $Hg(CNO)_2$, can be prepared in a similar manner from mercuric chloride and ammonium cyanate.

Mercury fulminate, $Hg(CNO)_2$, or perhaps $\left.\begin{matrix} C:N\cdot O \\ \| \qquad \\ C:N\cdot O \end{matrix}\right> Hg$, is an "isomeride" of mercuric cyanate (compare pp. 321 and 387). It is prepared by the action of nitric acid and alcohol on mercury. The crystals, which usually contain half a molecular proportion of water, possess the remarkable property that they can be compressed under a steady pressure, with only a very occasional explosion, but can then be detonated violently, and with very great certainty, by the prick of a needle. The sensitiveness of the DETONATOR produced by pressing the crystals into a copper shell depends on the density of the compressed mass, and can be almost completely destroyed by excessive pressure. For igniting gunpowder, the fulminate is mixed with potassium chlorate and antimony sulphide, since this mixture produces more flame than pure fulminate.

Mercuric oxide, HgO, also known as RED OXIDE OF MERCURY or RED PRECIPITATE, is formed on heating mercury at a temperature slightly below its boiling-point for several weeks in a glass vessel containing air; it is prepared on a large scale by heating a mixture of mercury and mercuric nitrate,

$$Hg + Hg(NO_3)_2 = 2HgO + 2NO_2.$$

When prepared in this way it forms a bright red crystalline powder; it can, however, be obtained as a yellow powder by adding potassium hydroxide to a solution of mercuric chloride,

$$HgCl_2 + 2KOH = HgO + H_2O + 2KCl;$$

it is therefore possible that mercuric oxide is dimorphous, like the iodide and sulphide. It is also noteworthy that mercuric oxide when heated becomes almost black in colour, but the original red colour of the oxide returns on cooling. Further heating decomposes it into mercury and oxygen,

$$2HgO = 2Hg + O_2.$$

When mercuric oxide is acted on by dilute ammonia it is converted slowly into a pale yellow powder having the empirical formula

$2HgO,NH_3,H_2O$, which explodes when heated (compare fulminating gold) and is known as MILLON'S BASE. When dried in a current of ammonia this loses water in several stages and is finally converted into **dimercuriammonium hydroxide,** $NHg_2 \cdot OH$, the parent substance from which the **dimercuriammonium chloride,** NHg_2Cl, of infusible and fusible white precipitates is derived; the **sulphate,** $(NHg_2)_2SO_4$, is formed when ammonia acts on mercuric sulphate, and the **iodide,** NHg_2I,H_2O (perhaps $O\left\langle {Hg \atop Hg} \right\rangle NH_2 \cdot I$), is formed as a brown precipitate by the action of ammonia on NESSLER'S REAGENT, a solution of potassium mercuri-iodide, K_2HgI_4, rendered alkaline with potassium hydroxide.

Mercuric hydroxide is not known, the precipitate obtained on adding an alkali hydroxide to a solution of a mercuric salt consisting of mercuric oxide.

Mercuric carbonate is also not known, but "basic carbonates" are formed on adding an alkaline carbonate to a solution of mercuric nitrate; these are probably mixtures, but substances having the composition $2HgO,HgCO_3$ and $3HgO,HgCO_3$ have been described.

Mercuric sulphide, HgS, occurs in beautiful red crystals as CINNABAR and is the principal ore of mercury (p. 877). It is obtained in a black form either by precipitating a solution of mercury with hydrogen sulphide, or by triturating mercury with sulphur, the ÆTHIOPS MINERALIS formerly used in pharmacy being obtained in this way.

It is prepared as a pigment on a large scale by heating the black sulphide, obtained by mixing mercury and sulphur, in retorts until it sublimes; the purest cinnabar condenses in the head of the retort, and is known as VERMILION. Vermilion of a finer colour is prepared by different wet processes, the colour varying considerably according to the mode of preparation.

Mercuric sulphide is insoluble in hot concentrated nitric acid or hydrochloric acid, but dissolves readily in aqua regia.

Mercuric sulphate, $HgSO_4$, is obtained by heating mercury with concentrated sulphuric acid, and crystallises from the strong acid in small silvery plates,

$$Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O.$$

It is decomposed by cold water, a lemon-coloured powder being precipitated, which is said to be a **basic sulphate,** $2HgO,HgSO_4$, compare $2HgO,HgCO_3$ and $2HgO,Hg(NO_3)_2$, but contrast with copper, the basic salts of which contain 3CuO (p. 841).

Mercuric nitrite, $Hg(NO_2)_2$, prepared by double decomposition from mercuric chloride and silver nitrite,

$$HgCl_2 + 2AgNO_2 = Hg(NO_2)_2 + 2AgCl,$$

crystallises in fine needles when the solution is evaporated in a vacuum. When heated it is decomposed mainly into mercurous nitrate and nitric oxide,

$$Hg(NO_2)_2 \quad = \quad HgNO_3 \quad + \quad NO,$$

although some mercuric oxide is also formed.

Mercuric nitrate, $Hg(NO_3)_2$, is formed when mercury is dissolved in an excess of nitric acid. By dissolving mercuric oxide in concentrated nitric acid, a syrupy liquid is obtained, from which on adding strong nitric acid a crystalline but deliquescent precipitate separates having the composition $Hg(NO_3)_2,H_2O$. This salt is decomposed by water at 25°, a heavy white precipitate being formed which is said to consist of the **basic nitrate,** $2HgO,Hg(NO_3)_2$; this is decomposed still further by heating with water, until finally mercuric oxide is obtained.

Detection and Estimation of Mercury.

Mercury can be detected readily in a compound or material containing it by heating a little of the dry substance with anhydrous sodium carbonate in a hard glass tube; **metallic mercury** sublimes and condenses in minute globules or as a film on the upper part of the tube.

A *mercurous salt* in solution gives with dilute hydrochloric acid a white precipitate of **mercurous chloride** (calomel) which is insoluble in boiling water or dilute acids and insoluble in ammonia, which, however, turns it black.

Mercuric salts give with hydrogen sulphide a black precipitate of **mercuric sulphide,** HgS, which is insoluble in boiling concentrated nitric acid, but dissolves in aqua regia; on concentrating the solution so as to remove the excess of acid and adding stannous chloride, a white precipitate of calomel is formed, or if an excess of stannous chloride be used, metallic mercury is precipitated as a black powder, which on boiling with hydrochloric acid forms globules of the metal.

Mercury is estimated quantitatively by precipitating as **mercuric sulphide,** HgS, or by distilling the material containing it in a glass tube with sodium carbonate, condensing the **metal** which is formed and weighing it. Mercury can also be estimated by depositing it electrolytically; very minute traces down to 1 part in 1000 million parts can be separated by this method and detected and roughly estimated by vaporising the mercury in a vacuum tube and examining it spectroscopically.

The atomic weight of mercury is based on determinations of the ratios of $HgCl_2$, $HgBr_2$, and HgC_2N_2 to Hg, Hg : 2Ag (by electrolysis) and $HgCl_2$: Hg : 2AgCl.

GALLIUM, INDIUM, AND THALLIUM.

31. Gallium.	Ga =	69·9.
49. Indium.	In =	114·8.
81. Thallium.	Tl =	204·0.

Classification.

The coinage metals and the three metals of the mercury group are followed in the periodic classification by the three elements cited above; these terminate the three transition series, in which iron, palladium, and platinum are the most familiar elements, and immediately precede the quadrivalent elements germanium, tin, and lead, which have already been described in the "typical series" of metals, thus,

29. Copper.	30. Zinc.	31. Gallium.	32. Germanium.
47. Silver.	48. Cadmium.	49. Indium.	50. Tin.
79. Gold.	80. Mercury.	81. Thallium.	82. Lead.

The dominant valency of the group is three, and the elements therefore show some points of analogy to aluminium and the tervalent elements of the earths, but they differ widely from them in many of their properties. Thus they are commonly found in nature as impurities in zinc blende and other sulphide ores, whilst aluminium and the metals of the earths are found almost exclusively in an oxidised condition, *e.g.*, as silicates and phosphates. The elements themselves are soft metals of low melting-point (30°, 155°, and 302°), whereas the metals of the earths melt at temperatures ranging from 600° to 1400°. The three elements also show the variable valency which is characteristic of the transition-series, in marked contrast with the rigid tervalency of most of the earths. Thus, gallium forms the chlorides, $GaCl_2$ and $GaCl_3$, indium gives InCl, $InCl_2$, and $InCl_3$, and thallium gives TlCl and $TlCl_3$. The most important salts of gallium and indium are tervalent, *e.g.*, sulphates of the type of the alums, but in the case of thallium the univalent salts are at least equally important. The three elements were all discovered by means of their spectra.

31. Gallium. Ga = 69·9.

This element, the properties of which were predicted, under the name of Eka-aluminium, by Mendeléeff in 1871, was discovered four years later, in zinc blende from the Pyrenees, by Lecoq de Boisbaudran, who gave to it the name it now bears (Latin, *Gallia*, France). Like lithium, it is very widely distributed and can be detected by two violet lines in its spectrum. Thus it is present in pig-iron from the Middlesbrough district and in flue-dust from the burning of coal in various localities. The element is a soft, tough, bluish-white metal, of density 5·9; it melts at 30·1°, but is capable of remaining in a superfused condition at atmospheric temperatures, and is not volatile at a red

heat. Its chemical properties resemble those of aluminium; thus it dissolves readily both in dilute hydrochloric acid and in aqueous potassium hydroxide, liberating hydrogen, but is attacked much less readily by dilute nitric acid.

The white **oxide**, Ga_2O_3, prepared as described below, is reduced by hydrogen to a gallous oxide, which dissolves in dilute sulphuric acid to form a salt which reduces potassium permanganate; the **hydroxide**, $Ga(OH)_3$, precipitated from an aqueous solution of a gallic salt, dissolves readily in potassium hydroxide, and less readily in ammonia. The **trichloride**, $GaCl_3$, prepared by the action of hydrogen chloride or of chlorine on the metal, is a soluble deliquescent salt, which melts at 75° and boils at 215°, giving a vapour which has at the boiling-point of sulphur a vapour density corresponding with the formula $GaCl_3$; metallic gallium reduces it to a **dichloride**, $GaCl_2$, melting at 164° and boiling at 535°. The **sulphate** forms an alum, $NH_4Ga(SO_4)_2,12H_2O$, and, like the **nitrate**, leaves a residue of the trioxide when ignited.

49. **Indium.** In = 114·8.

Indium was discovered in the zinc blende of Freiburg in 1863, by means of a strong indigo-blue line (of wave-length 4511) in its spectrum (Latin, *indicus*, Indian, compare indigo). The element is a soft, white, malleable metal of density 7·2; it melts at 155° but does not vaporise at 1450°. It is precipitated from its solutions (like lead) by the action of metallic zinc or by electrolysis, dissolves slowly in hydrochloric and in dilute sulphuric acids, and more readily in nitric acid.

The pale yellow **oxide**, In_2O_3, becomes darker in colour when heated (compare ZnO and HgO); unlike the oxide of gallium, it is only partially reduced when heated in a current of hydrogen, giving a black suboxide, perhaps InO. The **hydroxide**, $In(OH)_3$, is obtained as a gelatinous precipitate, which dissolves in potassium hydroxide, but not in ammonia. The **trichloride**, $InCl_3$, prepared by the action of chlorine on the metal, or of chlorine and charcoal on the oxide, is a soluble, deliquescent salt which hisses in contact with water, and yields a basic salt when the solution is evaporated (compare $AlCl_3$); the chloride sublimes below a red heat and its vapour-density corresponds with the formula $InCl_3$. The **dichloride**, $InCl_2$, prepared by the action of hydrogen chloride on the metal (compare $SnCl_2$), has a normal vapour-density at 1300°, and is decomposed by water as shown in the equation

$$3InCl_2 = 2InCl_3 + In.$$

When distilled over metallic indium it gives a **monochloride**, InCl, which is decomposed similarly by water. Three bromides and three iodides have also been prepared. Indium forms a soluble, deliquescent **nitrate** and **sulphate**; the latter gives an **alum**, $NH_4In(SO_4)_2,12H_2O$, which "melts in its water of crystallisation" at 36° and yields a **tetrahydrate**, $NH_4In(SO_4)_2,4H_2O$, to which type the sodium and potassium compounds likewise conform; the corresponding **acid sulphate**, $HIn(SO_4)_2,4H_2O$, has also been prepared (compare the rare earths, p. 669). The **sulphide**, In_2S_3, can be prepared as an infusible red mass by direct combination of the metal with sulphur, and

(unlike Al_2S_3) can also be thrown down from solution as a yellow precipitate, which dissolves in concentrated acids.

81. **Thallium.** Tl = 204·0.

This element was discovered by Crookes in 1861, whilst testing for tellurium in a seleniferous deposit from a sulphuric acid factory in the Harz. It was recognised by means of the brilliant green line (5351) in its spectrum, to which it owes its name (Greek, θάλλος, a green twig); thus a strong monochromatic green light can be produced by vaporising the chloride into the flame of a Bunsen burner. Like gallium and indium, thallium occurs generally in sulphide ores, but it also accompanies lithium in some micas, probably as a univalent metal. The element is a soft, white metal of density 11·9, resembling lead, which immediately follows it in the periodic classification. It undergoes a change of state at 226°, melts at 302°, boils at 1515°, and has a vapour-density corresponding with the formula Tl_2. It burns in air with a green flame, decomposes steam at a red heat, and dissolves readily in sulphuric and nitric acids, but less readily in hydrochloric acid. It forms univalent THALLOUS SALTS and tervalent THALLIC SALTS, but differs from gold in that the univalent salts are the more stable, in spite of the fact that gold is the first member and thallium the third member of an octave. The soluble thallous salts resemble those of potassium, with which they are usually isomorphous; the insoluble halides, sulphides, etc., resemble those of silver and lead. The thallic salts show some points of resemblance to the tervalent salts of alumina and the earths, although the analogy is far from complete.

Thallous oxide, Tl_2O, prepared by burning the metal in air or by dehydrating the hydroxide, is a black powder which melts at 300°; it dissolves in water to form the **hydroxide,** which crystallises out as the **dihydrate,** $TlOH,2H_2O$, has a strongly alkaline reaction, and absorbs carbon dioxide, forming a sparingly soluble **carbonate,** Tl_2CO_3; this loses carbon dioxide when heated above its melting-point. **Thallous chloride, bromide,** and **iodide** are formed by direct combination of the metal and halogen, and can be obtained as precipitates resembling the silver salts in colour, *e.g.*, TlCl is white, but becomes violet in the light, TlBr is pale yellow, and TlI bright yellow; the solubilities (0·3, 0·04, and 0·005 per cent. at 18°) are intermediate between those of the silver and lead salts. **Thallous fluoride** is soluble in water, compare AgF, and forms an acid salt, $TlHF_2$, compare KHF_2. **Thallous sulphide,** Tl_2S, is thrown down as a black precipitate in presence of acetic acid, but dissolves in mineral acids. **Thallous sulphate,** Tl_2SO_4, is isomorphous with K_2SO_4 and forms double salts of similar type, including $TlHSO_4,3H_2O$, $Tl_2Mg(SO_4)_2,6H_2O$ (compare schönite, p. 622), and the alum, $TlAl(SO_4)_2,12H_2O$. **Thallous nitrate,** $TlNO_3$, is a very soluble salt which resembles silver nitrate; it is trimorphous (rhombic, rhombohedral, and cubic), melts at 206° ($AgNO_3$ melts at 209°), and decomposes at higher temperatures.

Thallic oxide, Tl_2O_3, is a brown to black compound, prepared by igniting thallous nitrate, or by precipitation from an alkaline solution of a thallous

salt in presence of hydrogen peroxide; when heated it gives thallous oxide. **Thallic chloride,** $TlCl_3$, prepared from thallous chloride by the action of chlorine in presence of water, crystallises out as a tetrahydrate, and forms a series of double chlorides, including **thallous thallic chloride,** $Tl'_3Tl'''Cl_6$, compare Na_3AlF_6; the anhydrous salt, prepared by dehydrating the tetrahydrate, forms a **triammine,** $TlCl_3,3NH_3$.

Thallic sulphide, Tl_2S_3, is obtained by direct combination of the elements as a black product which is sufficiently plastic to be drawn into wire at summer temperatures, but becomes brittle below 12°.

The **sulphate,** $Tl_2(SO_4)_3,7H_2O$, forms a basic salt, $Tl(OH)SO_4,2H_2O$, an acid salt, $HTl'''(SO_4)_2,4H_2O$, double sulphates of the type $NH_4Tl'''(SO_4)_2,4H_2O$ and $KTl'''(SO_4)_2,4H_2O$ instead of alums, and an anhydrous **thallous thallic sulphate,** $Tl'Tl'''(SO_4)_2$.

CHAPTER XLV

RADIOACTIVE ELEMENTS

Atomic Number.	*Element.*	*Symbol.*		*Atomic Weight.*
86	Niton	Nt	=	222
87	—	—		—
88	Radium	Ra	=	226·0
89	Actinium	Ac	=	(226)
90	Thorium	Th	=	232·2
91	Protactinium	Pa	=	(230)
92	Uranium	U	=	238·2

General Properties of the Group.

The elements set out above represent the seventh period in the classification of the elements. This period, beginning with the gas niton, follows a period of 32 elements beginning with xenon. It has been suggested that it represents a fragment of another very long period of 32 elements. There are certain analogies to support this view, but as no elements of higher atomic weight than uranium are known, it is speculative; moreover, there is no indication of a cluster of tervalent elements, to correspond with the elements of the rare earths in period VI. The elements of period VII exhibit chemical properties which bring them into close relation with elements of lower atomic weights occupying corresponding positions in the earlier periods as follows:

Period.	Elements and Atomic Numbers.					
II	2 Helium	4 Beryllium	5 Boron	6 Carbon	7 Nitrogen	8 Oxygen
III	10 Neon	12 Magnesium	13 Aluminium	14 Silicon	15 Phosphorus	16 Sulphur
IV	18 Argon	20 Calcium	21 Scandium	22 Titanium	23 Vanadium	24 Chromium
V	36 Krypton	38 Strontium	39 Yttrium	40 Zirconium	41 Niobium	42 Molybdenum
VI	54 Xenon	56 Barium	57 Lanthanum	58 Cerium	73 Tantalum	74 Tungsten
VII	86 Niton	88 Radium	89 Actinium	90 Thorium	91 Protactinium	92 Uranium

These relationships are seen clearly in the chemical properties of the elements as described later in the chapter, but in each case the element of highest atomic weight is distinguished from its lower homologues by its radioactivity.

General Characteristics of the Radio-elements.

A RADIOACTIVE ELEMENT shows all the physical and chemical properties of a normal element, *e.g.*, it forms chemical compounds corresponding with its position in the periodic classification of the elements and gives a characteristic spectrum. It possesses, however, in addition the property of radioactivity, *i.e.*, of emitting radiations, depending on the fact that in any given interval of time a definite proportion of the atoms of the element disintegrates spontaneously, with the emission of certain types of radiation. This property belongs to the *atoms* and is not increased or decreased when these are combined with other atoms. Moreover, the rate of disintegration cannot be altered by any changes in the physical conditions, *e.g.*, of pressure or temperature, that have yet been tried.

The radio-elements include some forty elements possessing atomic weights which lie between 206 and 238·2. Above the limit of 208 there are no elements which are *not* radioactive. This fact suggests that atoms heavier than uranium atoms are not found, because if formed they are too unstable to persist. Only two of the radio-elements, uranium and thorium, were known before the discovery of radioactivity in 1896, and they are still the only ones which may be purchased in weighable quantities at a reasonable cost. The remainder exist in small amounts only, some being measured in grams, others in fractions of a milligram, and the majority in altogether unweighable quantities. At first sight it would appear that the investigation of the chemical properties of these elements would be almost a hopeless task, on account of the minuteness of the quantity of material available; nevertheless, owing to their unique property of radioactivity, these difficulties have been almost completely overcome, and the chemistry of nearly every radio-element has now been investigated experimentally.

Types of Radiation.

The radiations from radioactive substances are grouped under three heads.

(*a*) *The α-particle.*—This is the least penetrating of the three types of radiation. It carries two positive charges of electricity, has a mass of 4·00 (oxygen = 16), and is really a positively charged atom of helium (compare the positive rays of an *X*-ray bulb, which are positively charged atoms, or molecules, of the gas filling the bulb, p. 541). It is expelled by different radio-elements with different

velocities, all of which are of the order of one-twentieth of the velocity of light.

(b) *The β-particle.*—This is an electron, *i.e.*, a unit of negative electricity, like the cathode rays of an *X*-ray bulb, with an apparent mass of $\frac{1}{1830}$ of that of a hydrogen atom. β-particles are expelled with velocities ranging from 33 per cent. to 99 per cent. of that of light.

(c) *The γ-ray.*—This carries no charge, and, like the *X*-rays, is a wave-motion propagated with the velocity of light. It usually accompanies the emission of a β-particle, in much the same way as that in which cathode rays give rise to *X*-rays when they strike the anticathode.

Separation of Radio-elements.

The atom that remains after the expulsion of an α- or a β-particle is clearly different in nature from what it was before. It is a new atom, and the whole of the atoms resulting from these expulsions form a new element with chemical properties different from those of the parent element. This new element may be separated readily from the parent body by the ordinary methods of qualitative analysis as soon as its chemical reactions are known. Uranium atoms, for example, disintegrate with the expulsion of α-particles. The resultant body (known as uranium X_1) has an atomic weight of $238{\cdot}2 - 4 = 234{\cdot}2$ and may be separated quantitatively from uranium by taking advantage of its similarity to thorium. Thorium is most conveniently separated from uranium by precipitating it from a neutral solution with *m*-nitrobenzoic acid. To separate uranium X_1 from uranium therefore a little thorium nitrate is added to the solution prior to the precipitation with *m*-nitrobenzoic acid, when the precipitated thorium carries down with it the whole of the uranium X_1. If uranium X_1 existed in sufficient amount to allow of filtration, it would not be necessary to add the thorium to act as a nucleus in precipitating it.

Disintegration Series.

The study of radioactivity has led to the remarkable conclusion that one element produces another element on disintegration. This second element, if radioactive, produces a third, the third, if radioactive, a fourth, and so on, till finally an element is reached which does not disintegrate. A series of such elements is called a DISINTEGRATION SERIES, and at the present time three of these are known, the uranium, actinium, and thorium series. The heads of these series

92	Uranium	U	=	238·2
91	Protactinium	Pa	=	230 (?)
90	Thorium	Th	=	232·2

are known as PRIMARY RADIO-ELEMENTS.

Life of a Radio-element.

It has been stated that in a given interval of time a definite fraction of a radio-element disintegrates. This fraction, λ, is different for each radio-element, and is one of the most important constants of the element, since it determines the proportions of the element that may be expected to be present, *e.g.*, in a disintegrating mineral, and also the relative permanence of artificial preparations of the element. The disintegration of all radio-elements is expressed by the exponential relation

$$I_{t_2} = I_{t_1} e^{-\lambda(t_2 - t_1)}$$

where I_{t_1} is the number of atoms of a radio-element at time t_1 and I_{t_2} the number remaining at time t_2. From this equation we deduce

$$\lambda = \frac{\log I_{t_1} - \log I_{t_2}}{0{\cdot}4343\ (t_2 - t_1)},$$

where the logarithms are to the base 10.

The fraction λ is called the DISINTEGRATION CONSTANT and is determined experimentally. Its reciprocal is called the PERIOD OF AVERAGE LIFE of the atoms of the elements.

In a body which disintegrates according to the law expressed by the preceding equation, there is a definite interval of time at the end of which one-half of the number of atoms present at its commencement are still in existence. This interval is called the HALF-VALUE PERIOD. It may be deduced from the equation that the period of average life is 1·443 the half-value period.

Example.—For uranium X_1, $\lambda = 0{\cdot}0282$ per day. Period of average life $= \frac{1}{0{\cdot}0282} = 35{\cdot}5$ days. Half-value period $= \frac{35{\cdot}5}{1{\cdot}443} = 24{\cdot}6$ days.

In minerals which have not been weathered the relative amounts of different radio-elements are proportional to their half-value periods.

Example.—The half-value periods of uranium, radium, and uranium X_1 are 5×10^9 years, 1700 years, and 24·6 days respectively. In a uranium mineral containing 1 kilo. of uranium calculated as element there is therefore $\frac{1000 \times 1700}{5 \times 10^9}$ of a gram or 0·34 mg. of radium, and $\frac{1000 \times 24{\cdot}6}{5 \times 10^9 \times 365}$ of a gram or 0·000,013 mg. of uranium X_1, both measured as elements.

The Three Disintegration Series.

In the following tables are shown the members of the three disintegration series, their radiations, atomic weights, half-value periods, and the names of the elements chemically most similar to them.

TABLE 93.—THE URANIUM SERIES.

Element.	*Symbol.*	*Radiation.*	*At. wt.*	*Half-value Period.*	*Element chemically similar.*
Uranium 1 . .	U_1	α	**238·2**	5×10^9 Y	U
Uranium X_1 . .	UX_1	β,γ	234	24·6 D	Th
Uranium X_2 . .	UX_2	β,γ	234	1·15 M	Pa
Uranium 2 . .	U_2	α	234	About 10^6 Y	U
Uranium Y . .	UY	β	(230)	25·5 H	Th
Ionium . . .	Io	α	230	About 10^5 Y	Th
Radium . . .	Ra	α,β	**226**	1700 Y	Ra
Radium-emanation	Nt or RaEm	α	222	3·85 D	Nt
Radium A . .	RaA	α	218	3·0 M	Po
Radium B . .	RaB	β,γ	214	26·8 M	Pb
Radium C . .	RaC	(α) β,γ	214	19·5 M	Bi
Radium C′ . .	RaC′	α	214	10^{-6} S	Po
Radium C″ .	RaC″	β	210	1·4 M	Tl
Radium D . .	RaD	β,γ	210	16 Y	Pb
Radium E . .	RaE	β,γ	210	5·0 D	Bi
Radium F . . (Polonium)	Po or RaF	α	210	136 D	Po
Radium G . . (Uranium Lead)	RaG or Pb_U	In-active	**206·0**	—	Pb

(Y = years, D = days, M = minutes, S = seconds.)

The atomic weights shown in heavy type have been determined experimentally. All the others are calculated from that of radium, assuming that the α-particle weighs 4·00 units and neglecting the weight of the β-particle.

Notes on and Deductions from the Tables.

(*a*) *Character of Radiations.*—The radiations emitted by the various radio-elements have been determined by physical measurements, chiefly by means of the gold-leaf electroscope and with the help of absorbing screens. When an atom of a radio-element disintegrates, one α-particle, or one β-particle only, is emitted.

(*b*) *Nomenclature.*—The names of the elements were given by their

TABLE 94.—THE ACTINIUM SERIES.

Element.	*Symbol.*	*Radiation.*	*At. wt.*	*Half-value Period.*	*Element chemically similar.*
Protactinium . .	Pa	α	(230)	10^5 to 10^6 Y	Pa
Actinium . . .	Ac	β	226	About 20 Y	Ac
Radioactinium .	RaAc	α,β,γ	226	19 D	Th
Actinium X . .	AcX	α,β	222	11·5 D	Ra
Actinium-emanation	AcEm	α	218	3·92 S	Nt
Actinium A . .	AcA	α	214	0·002 S	Po
Actinium B . .	AcB	β,γ	210	36·1 M	Pb
Actinium C . .	AcC	$\alpha(\beta)$	210	2·15 M	Bi
Actinium C′ .	AcC′	α	210	0·005 S	Po
Actinium C″ . .	AcC″	β,γ	206	4·71 M	Tl
Actinium D . . (Actinium Lead)	AcD or Pb_{Ac}	Inactive	206	—	Pb

The atomic weights are calculated from that of protactinium. It is believed that this body is a disintegration product of UY; UY is a product either of U_1 or of U_2, probably the latter. If of the latter, the atomic weight of protactinium is 230; if of the former, its atomic weight is 234, and the other atomic weights must be increased by 4.

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discoverers and therefore before the whole disintegration series was unravelled. The nomenclature is accordingly neither completely systematic nor logical.

(*c*) *Branched Series.*—The arrows indicate the order in the disintegration series. U_2 probably gives two products, namely, Ionium, Io, and Uranium Y, UY. The former is in the direct series; the latter is called a "branch product" and is probably the parent of protactinium, Pa. RaC, AcC, and ThC also give two products on disintegration. The product in the direct series is formed when RaC and ThC expel a β-particle, and AcC an α-particle, and in the branch series when RaC and ThC expel an α-particle and Ac a β-particle. 99·97 per cent. of RaC forms RaC′ on disintegration, 99·85 per cent. of AcC forms AcC″, and 65 per cent. of ThC forms ThC′.

(*d*) *Half-value Periods.*—The half-value periods have been determined for the most part directly, *i.e.*, by separating the particular radio-element chemically, and measuring its rate of decay by an electroscope. In some cases the period has been measured by a method which involves the counting of the α-particles expelled in a given time by a known mass of the element.

TABLE 95.—THE THORIUM SERIES.

Element.	*Symbol.*	*Radiation.*	*At. wt.*	*Half-value Period.*	*Element chemically similar.*
Thorium . . .	Th ↓	α	**232·15**	About $1{\cdot}5 \times 10^{10}$Y	Th
Mesothorium 1 .	$MsTh_1$ ↓	β	228	6·7 Y	Ra
Mesothorium 2	$MsTh_2$ ↓	β,γ	228	6·2 H	Ac
Radiothorium .	RaTh ↓	α,β	228	1·9 Y	Th
Thorium X . .	ThX ↓	α	224	3·64 D	Ra
Thorium-emanation	ThEm ↓	α	220	54·5 S	Nt
Thorium A . .	ThA ↓	α	216	0·14 S	Po
Thorium B . .	ThB ↓	β,γ	212	10·6 H	Pb
Thorium C . .	ThC ↓	$(\alpha)\beta$	212	60·8 M	Bi
Thorium C′ . .	ThC′	α	212	10^{-11} S	Po
Thorium C″ .	ThC″	β,γ	208	3·1 M	Tl
Thorium D . . (Thorium Lead)	ThD or ↓ Pb_{Th}	Inactive	**208**	—	Pb

The atomic weights shown in heavy type have been determined experimentally. The others have been calculated from that of ThD.

The Ten Types of Radio-elements.

A remarkable fact comes to light when we examine the elements which possess chemical properties most similar to the radio-elements tabulated above, namely that although there are nearly 40 radio-

TABLE 96.—TYPES OF RADIO-ELEMENTS.

*Column of Periodic Table.**	*At. No.*	*Type.*	*Members of Group.*					
VI A . .	92	Uranium	—	—	Cr,	Mo,	W,	**U**
V A . .	91	Protactinium	—	—	V,	Cb,	Ta,	**Pa**
IV A . .	90	Thorium	C,	Si,	Ti,	Zr,	Ce(?)	**Th**
III A . .	89	Actinium	B,	Al,	Sc,	Yt,	La,	**Ac**
II A . .	88	Radium	Be,	Mg,	Ca,	Sr,	Ba,	**Ra**
O . .	86	Niton	He,	Ne,	Ar,	Kr,	Xe,	**Nt**
VI B . .	84	Polonium	O,	S,	Se,	Te,	**Po**	
V B . .	83	Bismuth	N,	P,	As,	Sb,	**Bi**	
IV B . .	82	Lead	C,	Si,	Ge,	Sn,	**Pb**	
III B . .	81	Thallium	—	—	Ga,	In,	**Tl**	

* A = first octave, B = last octave, of a long period.

elements, the number of chemical types which are represented is only ten. The atomic numbers, names, and positions in the periodic system of these ten TYPES OF RADIO-ELEMENTS are given in Table 96.

The first seven elements shown in heavy type are radio-elements, and, with the exception of thorium, are all found in pitchblende and other primary uranium minerals. Their positions in the periodic system have been established by an investigation of their chemical properties; thus protactinium (found in 1917) is the missing homologue of tantalum, actinium (found in 1899) is a homologue of lanthanum, radium (1898) is a homologue of barium, niton (1903) of the inert gases of the helium group, and polonium (1898) of tellurium.

Isotopes.

When the radio-elements which are chemically similar to any one of these ten types are examined, it is found that they not merely resemble one another in their chemical properties (as do the rare earths),

TABLE 97.—LIST OF ISOTOPES.

Atomic Number.	*Type.*	*Group.*	*Isotopes.*	*At. wt.*
81	Tl	IIIB	Tl	204·0
			AcC″	206
			ThC″	208
			RaC″	210
82	Pb	IVB	Pb	207·2
			RaG(Pb_U)	206
			AcD(Pb_{Ac})	206
			ThD(Pb_{Th})	208
			RaD	210
			AcB	210
			ThB	212
			RaB	214
83	Bi	VB	Bi	208·0
			RaE	210
			AcC	210
			ThC	212
			RaC	214
84	Po	VIB	Po	210
			AcC′	210
			ThC′	212
			RaC′	214
			AcA	214
			ThA	216
			RaA	218
85	[Eka-Iodine]	VIIB	—	—
86	Nt	O	Nt or	
			Ra Em	222
			Ac Em	218
			Th Em	220
87	[Eka-Cæsium]	IA	—	—
88	Ra	IIA	Ra	226·0
			AcX	222
			ThX	224
			MsTh 1	228
89	Ac	IIIA	Ac	226
			MsTh 2	228
90	Th	IVA	Th	232·2
			RaAc	226
			RaTh	228
			Io	230
			UY	230
			UX_1	234
91	Pa	VA	Pa	230
			UX_2	234
92	U	VIA	U_2	234
			U_1	238·2

but that their chemical and physical properties are apparently identical. Thus they show identical chemical reactions and give identical X-ray spectra; their arc-spectra are also similar, and show differences of wave-length which are only of the order of 1 part in 100,000. The elements of each type therefore differ only in their

atomic weights and in their radioactive properties. Such bodies are referred to as ISOTOPES (p. 540), this word implying that they occupy "the same place" in the periodic table.

For convenience of reference the radio-elements are shown in Table 97 as groups of isotopes, with their symbols, atomic numbers, atomic weights, and positions in the periodic system.

Separation of Radioactive Types.

Since the chemical behaviour of isotopic bodies is absolutely the same as that of the type, it follows :

(i) That *if two or more isotopes are mixed they cannot be separated by ordinary chemical methods.* For example, Mesothorium 1 and radium when mixed cannot be separated, nor can ionium and thorium, nor Uranium 1 and Uranium 2, nor can lead be separated from RaB, RaD, RaG, AcB, AcD, ThB, or ThD.

(ii) That *a radio-element can be separated from a preparation or a mineral by adding a small quantity of the type-element and then proceeding as though the type-element alone were being separated from the constituents of the mineral or preparation.* Thus RaB may be separated from RaC or ThB from ThC by adding to the solution small amounts of soluble salts of lead and bismuth ; the lead is then separated from bismuth in the ordinary way and carries with it the RaB and ThB, whilst the bismuth fraction contains the RaC or ThC. The separation of UX_1 from U by the addition of thorium has already been mentioned.

When the type element is itself rare, the next lower member of the group is used instead. Thus protactinium was separated from pitchblende residues by adding a soluble salt of tantalum and separating the tantalum from the other elements by the ordinary methods. Protactinium resembles tantalum sufficiently to be separated with it in this way. In the same way, radium is separated from uranium minerals, and mesothorium 1 from thorium minerals, by adding small quantities of a soluble barium salt to a solution of the mineral and separating out the barium. Again, mesothorium 2, which is an isotope of actinium and therefore similar to lanthanum, may be separated from mesothorium 1, which is an isotope of radium and therefore similar to barium, by adding lanthanum and barium to the mixed solution and precipitating the former with ammonia.

The Periodic System and the Radio-elements.

It has been shown above that the hypothesis of isotopes allows of the inclusion of the whole of the radio-elements in the periodic system of classification. It now remains to show that there is a very simple relation between the position of a radio-element in the periodic table

and the radiation expelled by the element of which it is the product. This relation may be expressed thus :

(i) *When an element expels an α-particle* (carrying two positive charges) *its atomic number is diminished by* 2, *i.e.*, the product occupies a position in the periodic system two places lower than the parent element.

(ii) *When an element expels a β-particle* (carrying one negative charge) *its atomic number is increased by* 1, *i.e.*, the product occupies a position one place higher in the table than the parent element.

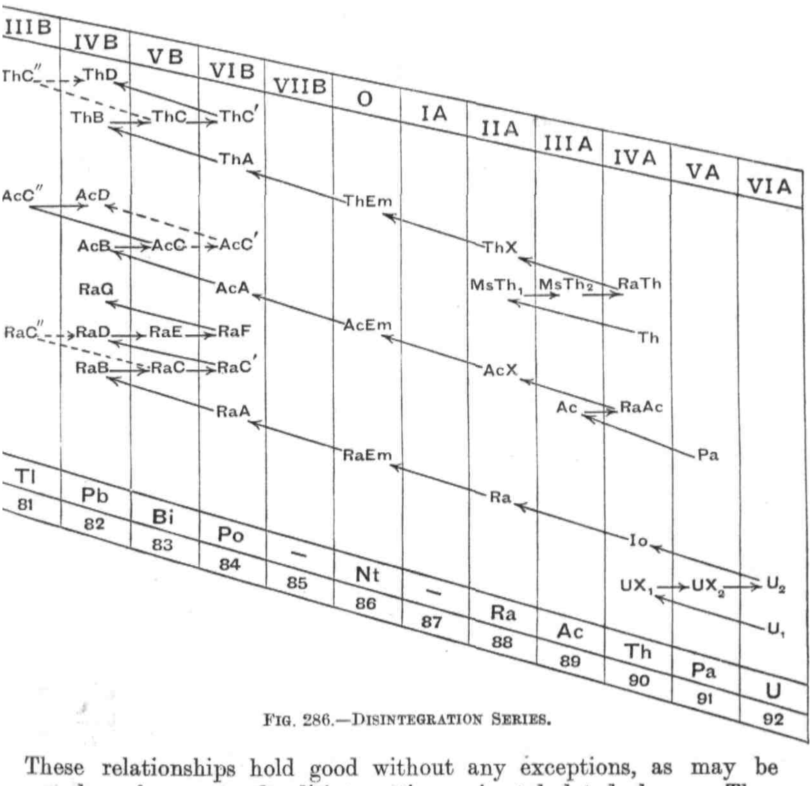


FIG. 286.—DISINTEGRATION SERIES.

These relationships hold good without any exceptions, as may be seen by reference to the disintegration series tabulated above. They are shown graphically in Fig. 286, in which the three disintegration series are set out together.

The Structure of the Atom.

The relationships of the last paragraph were deduced empirically from consideration of the chemical properties of those radio-elements

which had then been investigated. They may, however, also be deduced from the theory of the structure of the atom which is accepted at the present time. According to this theory (p. 544) the atom consists of a small NUCLEUS which contains practically the whole of the mass of the atom, and has a charge of positive electricity equal to some multiple of the charge on an electron; surrounding the nucleus are rings of ELECTRONS, the number of electrons being identical with the excess of positive charges on the nucleus, so that the atom is electrically neutral. The charge on the nucleus determines the number and the behaviour of the planetary electrons in the neutral atom, and in the ions derived from it by gain or loss of electrons, and therefore fixes the chemical nature of the element. In the case of isotopes the atoms have nuclei which carry the same positive charge and are balanced by the same number of planetary electrons; they therefore exhibit the same chemical properties. The actual amounts of positive and negative electricity in the nucleus may, however, be different for each member of a series of isotopes, giving rise to atoms of different atomic weights, although the net positive charges are the same throughout. The charges which make up the nucleus are not affected by ordinary chemical and physical processes, which merely cause some of the planetary electrons to vibrate, or, as in ionisation, give rise to an increase or decrease in the number of electrons in the outer rings. Radioactive disintegration, on the other hand, involves a change in the nucleus, from which both α- and β-particles may be expelled. This nucleus is inaccessible in all ordinary chemical and physical operations, but if a process could be devised which would get at the nucleus and rupture it, it might then be possible either to accelerate the disintegration of a radio-element, or to disintegrate elements which are not normally radioactive. The latter process has apparently been accomplished in the case of nitrogen, which when bombarded with α-particles from Radium C′ gives atoms having the same mass as hydrogen.

Description of the Radioactive Types.

Of the ten radioactive types, namely,

III	IV	V	VI	0	II	III	IV	V	VI
81	82	83	84	86	88	89	90	91	92
Tl	**Pb**	**Bi**	Po	Nt	Ra	Ac	**Th**	Pa	**U**

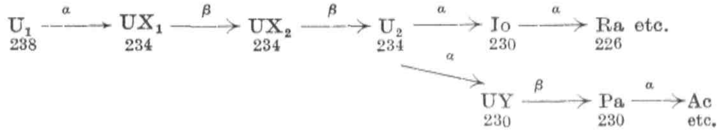
the first three elements are not radioactive and have been described as normal members of their respective families. Two others, namely, thorium and uranium, which have a very long "average life" and are therefore only slightly radioactive, have also been described as the highest homologues of the families to which they belong. There are therefore only five types, discovered by means of their radioactivity and not previously known, of which a description must now be given.

91. **Protactinium.** Pa = 230 (?).

(*a*) *Discovery.*—It was known that actinium is in some way a branch-product of uranium, and, since its atomic number is 89, the atomic number of its parent must be either 91 or 88, according as the parent emits an α- or a β-particle. In the former case the parent of actinium should be similar to tantalum. A soluble tantalum salt was therefore added to a large quantity of pitchblende residues and when separated and purified was found to contain a body which on disintegration gave actinium. This body was therefore the parent of actinium and was named protactinium by Hahn, who discovered it in this way. The existence of this body was also proved by Soddy, who heated pitchblende in an atmosphere of carbon tetrachloride under conditions in which Ta_2O_5 was volatilised. Actinium appeared gradually in the sublimate, which therefore contained its parent element.

(*b*) *Occurrence.*—Protactinium occurs only in uranium minerals.

(*c*) *Chemical Properties.*—Nothing is definitely known at present about its chemical properties, except that it resembles tantalum, of which it is evidently the homologue. Since it is an element with a long period of life, it exists in weighable quantities, and as soon as methods for separating it from pitchblende in quantity have been worked out, its chemical properties and atomic weight, etc., may be determined by the usual methods. The atomic weight is taken provisionally as 230, *i.e.*, 8 units less than uranium, because it is considered that its position in the disintegration series is probably as set out below :



89. **Actinium.** Ac = 226 (?).

(*a*) *Discovery.*—Debierne in 1899, while working up uranium residues, discovered an element which was precipitated from solution by ammonia and yet was distinct in its radioactivity from thorium. Giesel in 1902 separated a very active substance from pitchblende along with the rare earths; after further fractionation the new body was associated mainly with lanthanum. This body and that discovered by Debierne were found to be the same.

(*b*) *Occurrence.*—Actinium, like its parent protactinium, occurs in all uranium minerals and there only.

(*c*) *Chemical Properties.*—The chemical properties of actinium resemble those of the rare earths, and particularly of lanthanum; but when fractionated along with rare earths, it appears to be concentrated in the neodymium and samarium fractions, so that in the serial order of the rare-earth elements it would occupy a position between these two metals, viz., 57 La, 58 Ce, 59 Pr, 60 Nd, **Ac**, 62 Sm, 63 Eu, 64 Gd, etc., *i.e.*, it appears to be a homologue of the missing element of atomic number 61. Other experiments show that it is intermediate between lanthanum and calcium in chemical properties. In qualitative analysis it is precipitated as hydroxide by ammonia, but quantitatively only in the absence of ammonium salts; its oxide is therefore more strongly basic than that of aluminium. It resembles lanthanum in

that it is precipitated as oxalate by oxalic acid or by ammonium oxalate, but not quantitatively when mineral acids are present. It is not precipitated from solutions of the chloride by sodium thiosulphate, nor from a nitrate-solution by hydrogen peroxide, so that it is easily separated from thorium. Like the rare earths, it is precipitated quantitatively by aqueous hydrofluoric acid. It is precipitated along with manganese when that element is precipitated from basic solutions as a manganite.

88. **Radium.** Ra = 226·0.

(*a*) *Discovery.*—In their pioneer work on radioactivity in 1898, M. and Mme. Curie found that radioactive minerals containing uranium were many times more active than they would have been if their radioactivity had been due to uranium alone, even if the mineral had contained nothing but pure uranium compounds. It was natural to suppose, therefore, that other and more powerfully radioactive substances were present. In a chemical examination of pitchblende they separated the substance now known as radium along with the barium of the mineral.

(*b*) *Occurrence.*—Radium, being a disintegration product of uranium, is found in all uranium minerals (p. 749), and in a constant ratio to the amount of uranium present, namely about one part in three million, provided the minerals are sufficiently old and that they have not been weathered. CARNOTITE, or potassium uranyl vanadate, $K(UO_2)VO_4,1\frac{1}{2}H_2O$, a mineral found in Colorado and Utah, is the chief source of radium at present. AUTUNITE, or calcium uranyl phosphate, $Ca(UO_2)_2(PO_4)_2,8H_2O$, is not so good a source as carnotite or pitchblende, because it usually contains only 25 to 70 per cent. of the equilibrium-amount of radium.

(*c*) *Separation from Minerals.*—(i) The barium is separated from a solution of the mineral, or from its residues, by the usual chemical methods (If the mineral contains little or no barium, a small quantity of a soluble barium salt is added to it and the barium separated out later.) The whole of the radium associates itself with the barium, which it resembles very closely.

(ii) Since there is no reagent known which precipitates one of these elements quantitatively and leaves the other in solution, the radium is separated from the barium by repeated fractional crystallisation of the chlorides, or of the bromides, the halogen salts of radium being less soluble in water and in mineral acids than the corresponding salts of barium. The picrates, bromates, and ferrocyanides have also been proposed as suitable materials for fractionation, but crystallisation of the chlorides is considered the most satisfactory process.

(*d*) *Metallic radium* has been prepared by a method similar to that employed in the preparation of metallic barium (p. 645). Liquid radium-amalgam was prepared by electrolysing about 0·1 gram of radium chloride with a mercury cathode. The amalgam was distilled in hydrogen under reduced pressure. At 700° the last of the mercury was volatilised, leaving the radium as a pure white metal. It melts at about 700°.

(*e*) *Compounds of Radium.*—The chief compounds of radium are :

Radium hydroxide	$Ra(OH)_2$
,, chloride	$RaCl_2$ and $RaCl_2,2H_2O$
,, bromide	$RaBr_2$ and $RaBr_2,2H_2O$
,, nitrate	$Ra(NO_3)_2$
,, sulphate	$RaSO_4$
,, carbonate	$RaCO_3$.

The chemical properties and appearance of these compounds are very similar to those of the corresponding barium salts. The sulphate, the hydrated chloride, and the hydrated bromide are the commonest salts. The sulphate is ten times less soluble than barium sulphate; $RaCl_2,2H_2O$ is less soluble in dilute hydrochloric acid than $BaCl_2,2H_2O$, and $RaBr_2,2H_2O$ is less soluble in dilute hydrobromic acid than $BaBr_2,2H_2O$. The carbonate dissolves readily in hydrochloric acid.

The action of the radiations emitted by radium must not be forgotten when preparing its salts. The water in a moist preparation is decomposed gradually into its elements, and if such a preparation be sealed up an accident may result. The bromide gives off bromine in the air, forming the hydroxide. The safest preparation to deal with is the sulphate, since it is stable, and can be kept dry, and, if at any time a radium-solution is required, the sulphate may be decomposed by fusion with alkaline carbonates and the radium carbonate which results dissolved in hydrochloric acid. Salts of radium colour the flame carmine.

86. **Niton.** Nt = 222.

The three isotopic emanations show very similar physical properties and, apart from their radioactivity, behave very similarly to argon, krypton, and xenon. Radium emanation, or niton, having the longest period of average life, has been most studied. It has a density of 111; it boils at $-65°$; its critical temperature is $104·5°$; its coefficient of diffusion into air at normal temperature and pressure is 0·1; its absorption-coefficient in water is 0·30.

In a mineral or a solid preparation of radium the emanation is occluded and very little of it escapes. By heating the mineral or preparation strongly, varying quantities may be obtained. By dissolving the preparation, heating the solution, and either bubbling air through it or pumping off the gases, the emanation may be expelled completely. The emanation condenses at low pressures at $-150°$, and this property is made use of in its purification.

The amount of emanation in equilibrium with 1 gram of radium (element) is 0·59 cub. mm. The corresponding values of the volumes of thorium and actinium emanations in equilibrium with their parents may be calculated from the half-value periods, but are extremely small.

84. **Polonium.** Po = 210.

(*a*) *Discovery.*—Polonium was discovered by M. and Mme. Curie in pitchblende, from which it was separated with the bismuth in the mineral. The name was given in honour of the country in which Mme. Curie was born.

(*b*) *Occurrence.*—Polonium does not exist in weighable amount, owing to its short half-value period of only 136 days as compared with 5×10^9 years for uranium and 1700 years for radium. Thus if 50,000 kilograms of a mineral containing 60 per cent. of uranium calculated as element were worked up the maximum amount of polonium obtainable would only be

$$\frac{50{,}000 \times 1000 \times 0·6 \times 136}{5 \times 10^9 \times 365}, \text{ i.e., } 0·0022 \text{ of a gram.}$$

Experimental determination of its chemical properties in detail, its spectrum, and its atomic weight is therefore possible only after its separation from very large quantities of pitchblende or carnotite. In the laboratory traces of polonium may be recovered from an old radium preparation which has been

sealed up for some time, or from tubes in which large quantities of emanation have decayed.

(c) *Chemical Properties.*—Polonium resembles tellurium more closely than any other element. It is also like bismuth. When minerals are worked up for polonium, it is precipitated by sulphuretted hydrogen in acid solution, but may be separated from bismuth by fractional precipitation of the basic nitrate with water, or of the sulphide by hydrogen sulphide from solutions made very acid with hydrochloric acid, and by sublimation in a vacuum. The metal may be separated from bismuth by immersing a plate of silver in a solution of the two elements in hydrochloric acid, when the polonium is deposited quantitatively on the plate. If stannous chloride be added to a solution in hydrochloric acid of polonium and impurities, the polonium and the tellurium alone are precipitated. If now these bodies are dissolved to form not too acid a solution, the tellurium can be precipitated by adding hydrazine hydrate, and the polonium which remains in solution can then be precipitated by stannous chloride.

In the laboratory, polonium is always separated by immersing a plate of silver, copper, nickel, or bismuth in a solution containing polonium. As much as 95 per cent. of the whole can be deposited on the plate. If RaD or RaE are simultaneously deposited, the polonium can be freed from them easily by volatilisation.

TABLE 98.—ATOMIC NUMBERS AND ATOMIC WEIGHTS.

Atomic number.	Name.	Symbol.	Atomic weight.
13.	Aluminium	Al	27·1
51.	Antimony	Sb	120·2
18.	Argon	A	39·9
33.	Arsenic	As	74·96
56.	Barium	Ba	137·37
4.	Beryllium	Be	9·1
83.	Bismuth	Bi	208·0
5.	Boron	B	10·9
35.	Bromine	Br	79·92
48.	Cadmium	Cd	112·40
55.	Cæsium	Cs	132·81
20.	Calcium	Ca	40·07
6.	Carbon	C	12·005
58.	Cerium	Ce	140·25
17.	Chlorine	Cl	35·46
24.	Chromium	Cr	52·0
27.	Cobalt	Co	58·97
41.	Columbium	Cb	93·1
29.	Copper	Cu	63·57
66.	Dysprosium	Dy	162·5
68.	Erbium	Er	167·7
63.	Europium	Eu	152·0
9.	Fluorine	F	19·0
64.	Gadolinium	Gd	157·3
31.	Gallium	Ga	70·1
32.	Germanium	Ge	72·5
79.	Gold	Au	197·2
2.	Helium	He	4·00
67.	Holmium	Ho	163·5
1.	Hydrogen	H	1·008
49.	Indium	In	114·8
53.	Iodine	I	126·92
77.	Iridium	Ir	193·1
26.	Iron	Fe	55·84
36.	Krypton	Kr	82·92
57.	Lanthanum	La	139·0
82.	Lead	Pb	207·20
3.	Lithium	Li	6·94
71.	Lutecium	Lu	175·0
12.	Magnesium	Mg	24·32
25.	Manganese	Mn	54·93
80.	Mercury	Hg	200·6
42.	Molybdenum	Mo	96·0
60.	Neodymium	Nd	144·3
10.	Neon	Ne	20·2
28.	Nickel	Ni	58·68
86.	Niton	Nt	222·4
7.	Nitrogen	N	14·008
76.	Osmium	Os	190·9
8.	Oxygen	O	16·00
46.	Palladium	Pd	106·7
15.	Phosphorus	P	31·04
78.	Platinum	Pt	195·2
19.	Potassium	K	39·10
59.	Praseodymium	Pr	140·9
88.	Radium	Ra	226·0
45.	Rhodium	Rh	102·9
37.	Rubidium	Rb	85·45
44.	Ruthenium	Ru	101·7
62.	Samarium	Sa	150·4
21.	Scandium	Sc	45·1
34.	Selenium	Se	79·2
14.	Silicon	Si	28·3
47.	Silver	Ag	107·88
11.	Sodium	Na	23·00
38.	Strontium	Sr	87·63
16.	Sulphur	S	32·06
73.	Tantalum	Ta	181·5
52.	Tellurium	Te	127·5
65.	Terbium	Tb	159·2
81.	Thallium	Tl	204·0
90.	Thorium	Th	232·15
69.	Thulium	Tm	168·5
50.	Tin	Sn	118·7
22.	Titanium	Ti	48·1
74.	Tungsten	W	184·0
92.	Uranium	U	238·2
23.	Vanadium	V	51·0
54.	Xenon	Xe	130·2
70.	Ytterbium	Yb	173·5
39.	Yttrium	Yt	89·33
30.	Zinc	Zn	65·37
40.	Zirconium	Zr	90·6

TABLE 99.—AVERAGE COMPOSITION OF THE LITHOSPHERE (F. W. CLARKE).

	Igneous rocks (95%)	Shale (4%).	Sandstone (0·75%).	Limestone (0·25%).	Weighted average.
SiO_2	**59·83**	**58·10**	**78·33**	5·19	59·77
Al_2O_3	**15·02**	**15·40**	4·77	0·81	14·89
Fe_2O_3	2·62	4·02	1·07	0·54	2·69
FeO	3·43	2·45	0·30	—	3·39
MgO	3·74	2·44	1·16	7·89	3·74
CaO	4·83	3·11	5·50	**42·57**	4·86
Na_2O	3·37	1·30	0·45	0·05	3·25
K_2O	3·05	3·24	1·31	0·33	2·98
H_2O	1·90	5·00	1·63	0·77	2·02
TiO_2	0·79	0·65	0·25	0·06	0·77
ZrO_2	0·023	—	—	—	0·02
CO_2	0·49	2·63	5·03	**41·54**	0·70
P_2O_5	0·29	0·17	0·08	0·04	0·28
S	0·10	—	—	0·09	0·10
SO_3	—	0·64	0·07	0·05	0·03
Cl	0·063	—	—	0·02	0·06
F	0·10	—	—	—	0·09
BaO	0·10	0·05	0·05	—	0·09
SrO	0·043	—	—	—	0·04
MnO	0·10	—	—	0·05	0·09
NiO	0·026	—	—	—	0·025
Cr_2O_3	0·048	—	—	—	0·05
V_2O_3	0·026	—	—	—	0·025
Li_2O	0·011	—	—	—	0·01
C	—	0·80	—	—	0·03

TABLE 100.—AVERAGE COMPOSITION OF KNOWN TERRESTRIAL MATTER (F. W. CLARKE).

	Lithosphere (93%).	Hydrosphere (7%).	Average including atmosphere.
O	47·33	85·79	50·02
Si	27·74	—	25·80
Al	7·85	—	7·30
Fe	4·50	—	4·18
Ca	3·47	0·05	3·22
Mg	2·24	0·14	2·08
Na	2·46	1·14	2·36
K	2·46	0·04	2·28
H	0·22	10·67	0·95
Ti	0·46	—	0·43
C	0·19	0·002	0·18
Cl	0·06	2·07	0·20
Br	—	0·008	—
P	0·12	—	0·11
S	0·12	0·09	0·11
Ba	0·08	—	0·08
Mn	0·08	—	0·08
Sr	0·02	—	0·02
N	—	—	0·03
F	0·10	—	0·10
All other elements	0·50	—	0·47

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